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UNIVERSITY OF ALBERTA

QUANTITATIVE RELATIONSHIPS FOR THE REMOVAL OF BIODEGRADABLE ORGANIC MATTER AND RELATED PARAMETERS IN BIOLOGICAL DRINKING WATER TREATMENT

by

© M. Jillian Mitton

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of
the requirements for the degree of
Master of Science

in

Environmental Engineering

Department of Civil Engineering

Edmonton, Alberta

Fall 1993

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of Canada

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ISBN 0-315-88442-8

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "Quantitative Relationships for the Removal of Biodegradable Organic Matter and Related Parameters in Biological Drinking Water Treatment" submitted by M. Jillian Mitton in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering.

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Abstract

Biological water treatment has been shown to effectively remove biodegradable organic matter, chlorinated by-product precursors and ozonation by-products. This thesis research demonstrates that the removal rate of biodegradable organic carbon (BDOC), assimilable organic carbon (AOC) and many disinfection by-products is linearly related to the influent concentration, suggesting removal rates can be described by a first-order process. This study focuses on results from a pilot plant study in Edmonton, Alberta and compares results from five other biological water treatment studies where different water sources and operating conditions were experienced.

For Total Organic Carbon (TOC), Chlorine Demand, Haloacetic Acid Formation Potential (HAAFP), Trihalomethane Formation Potential (THMFP), and Adsorbable Organic Halide Formation Potential (AOXFP), a single apparent first-order rate constant can be used to describe the removal. Comparisons with another cold water study displayed the same linearity and a similar first-order rate constant. For these parameters, the calculated apparent rate constants were dependent on empty bed contact time (EBCT).

The analysis of aldehydes revealed that their removal rate is also linearly related to influent concentration. For formaldehyde a single apparent first-order rate constant can be used to describe approximately the removal where operating conditions were similar. For methyl glyoxal, glyoxal, acetaldehyde and propanal, poor linearity was displayed and where reasonable linearity was observed the mechanism for removal was suspected to also include adsorption.

For the removal of AOC, BDOC, HAAFP, and formaldehyde, excellent linearity was displayed for removal rates versus influent concentrations in every study investigated. TOC, Chlorine Demand, THMFP and AOXFP displayed good linearity, particularly in second stage biological filtration. The apparent first-order rate constants were dependent on operating conditions, and a non-linear relationship was found between apparent rate constant and EBCT. It was found that the x-intercept or the minimum achievable concentration varied between studies and operating conditions. This apparent rate constant shows promise as an initial approximate design tool for biological drinking water treatment to remove biodegradable organic matter, chlorinated by-product precursors, and at least some ozonated by-products

Acknowledgments

The author wishes to thank a number of people who in various ways made valuable contributions to this study:

Michèle Prévost, now at École Polytechnique and formerly the R & D Manager at GL Consultants, for providing data from a Laval, Quebec biological drinking water study.

Richard Miltner, at the U.S. Environmental Protection Agency, for providing data from a Cincinnati, Ohio study.

Dr. David Reckhow, at the Civil Engineering Department, University of Massachusetts, for providing data from a Woodbridge, CT Study.

Stuart W. Krasner, from the metropolitan Water District of Southern California, for providing aldehyde and AOC data for a Southern California Study.

Olivier LeBrun and Maria Demeter, who performed the chemical analyses for this research.

Janis Cook, who performed the AOC analysis, and also assisted the operator during water sampling events.

Ph D student Shulin Zhang, whose cooperation and advice was appreciated throughout this study.

AWWARF for the opportunity to be involved with this biological drinking water study.

Finally, the author wishes to thank Dr. Peter M. Huck for his advice and guidance during this study.

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List of Abbreviations and Symbols

BOM - Biodegradable Organic Matter

TOC - Total Organic Carbon

NVOC - Non Volatile Organic Carbon

DOC - Dissolved Organic Carbon

AOC - Assimilable Organic Carbon

BDOC - Biodegradable Organic Carbon

HAAFP - Haloacetic Acid Formation Potential

DCAAFP - Dichloroacetic Acid Formation Potential

TCAAFP - Trichloroacetic Acid Formation Potential

AOXFP - Adsorbable Organic Halogen Formation Potential

THMFP - Trihalomethane Formation Potential

CHFP - Chloral Hydrate Formation Potential

EBCT - Empty Bed Contact Time

GAC - Granular Activated Carbon

S_{min} - Minimum allowable concentration of rate limiting substrate for steady state biofilm, milligrams per liter

K_s - Substrate concentration at which rate is half the maximum (Monad Kinetics), milligrams per liter

Y - True yield coefficient, milligram cells per milligram

b' - Total biofilm loss rate coefficient, liters per day.

J - Flux of a substrate into the surface of the biofilm

Ss - Substrate concentration at surface of biofilm

NOM Natural Organic Matter

CHAPTER 1.0
INTRODUCTION

1.1 History

The objective of water treatment practice is to provide a water safe for human consumption and industrial use at a realistic cost. Biological water treatment has been recognized as being effective for removing organic material, ammonia, nitrate, iron and manganese (Bouwer and Crowe, 1988).

A considerable amount of attention has been given in the past two decades to the phenomenon of biological activity in granular activated carbon (GAC) columns. The term most often used to describe this treatment phenomenon is biological activated carbon (BAC). Many of the advantages of biological activated carbon were first recognized in the 1960's by German water treatment scientists in drinking water plants along the Rhine River in the Dusseldorf area (Rice et al, 1978). Subsequently, BAC processes have been studied and implemented in Switzerland, France, Holland, Belgium, Germany and most recently the United Kingdom (Rice et al, 1978). In the United States, the US Environmental Protection Agency Water Supply Research Laboratory in Cincinnati, Ohio, began testing pilot GAC columns in the late 1976. Since then, numerous studies have been completed and reported in the literature (e.g. van der Kooij et al., 1982, Janssens et al, 1984, Gerval and Bablon, 1987 and van der Kooij et al., 1989).

The contamination of water supplies by non-point sources, including organic and inorganic compounds, in addition to pathogens such as protozoa and viruses are of current concern with respect to water treatment practices. Of significant importance, is the wide occurrence of synthetic organic compounds (SOC's and pesticides) and nitrogen species through the use of fertilizer. Their loadings to surface and groundwaters have provided additional challenges to current water treatment facilities. Biological treatment offers a potential alternative to relatively costly, and in some cases ineffective physiochemical treatment processes, for the removal of organic contaminants, nitrogen species, iron and manganese (Bouwer and Crowe, 1988).

Of great concern to the water treatment industry is the formation of chlorinated disinfection by-products through the reaction of chlorine with dissolved organic matter. A growing concern has developed with the formation of ozonation by-products, since ozone is most often used as an oxidant in biological drinking water practice. The chlorinated disinfection by products, in particular the trihalomethanes (THM's), and ozonated by-products, particularly formaldehyde, are either known or suspected to be carcinogenic in animal laboratory studies. In Canada, concern about the possible effects of disinfection by-products on human health has lead to proposed stricter regulations for THMs. Therefore in some cases the production of high quality drinking water requires techniques for effective removal of dissolved organics prior to the application of chlorine.

As will be discussed in the literature review, numerous pilot and full scale biological treatment studies have been conducted throughout North America. They have focused on the removal of biodegradable organic matter (BOM), chlorinated disinfection by-product precursors and ozonation by-products. Effort is also being expended to model the biofilm kinetics for the removal of BOM. Another approach was taken by Huck and Anderson (1992), who first reported that an empirical modeling approach could be used to predict the removal of BOM and related parameters. They noted that when the removal rates for several parameters were plotted against the influent concentrations, a linear pattern was observed. This suggested that this relationship could be modeled as a first order process, and an apparent first-order rate constant calculated. This simple approach shows promise for further development into an easy modeling technique for general application. Due to the complexity of most biofilm models there is need for a simpler relationship for practical applications in preliminary design, and to provide confirmatory results to solutions obtained with the intricate biofilm models. The purpose of this thesis research was to further investigate the empirical modeling technique and apply it to different waters and operating conditions to determine its feasibility.

1.2 Objectives

The objectives for this thesis are outlined below:

1. To obtain raw data, from a previous Edmonton 1989-1990 study, and the current Edmonton study. In addition, to obtain data from other pilot plants representing different operation conditions and different water sources: Woodbridge, Connecticut, Southern California, Laval, Quebec and Cincinnati, Ohio.

2. To conduct the empirical modeling approach for data obtained from every study. This analysis would include biodegradable organic matter (BOM), chlorinated by product precursors, and ozonated by-products. Individual parameters would be analyzed to determine an apparent rate constant, and x-intercept to indicate the minimum achievable effluent concentration for each parameter. Statistical testing would be conducted to determine significance and 95% confidence intervals. Regression residuals would be analyzed and Lack of Fit Tests would be performed on individual parameters for every study.

3. To compare results from all studies for each individual parameter. The classes of compound, will also be compared and discussed.

4. To correct the apparent rate constants for temperature. This correction will be attempted both quantitatively and qualitatively.

5. To demonstrate the usefulness of this modeling technique by showing an example, where the removal efficiencies for various seasonal conditions are predicted for various parameters. This will also demonstrate which parameters would be limiting, in terms of operating conditions, and will assist in determining cost effective options.

CHAPTER 2
LITERATURE REVIEW

2.1 Fundamentals of Biological Processes

Huck and Rittmann (1989) recognized several advantages to biological treatment, which are given as follows; a) effective removal of organic and inorganic substances, b) reduction of potential regrowth in distribution systems, c) reduction in chlorine demand and d) compared to other treatments, a biological treatment system is simple to construct and operate.

The rational for biological drinking water treatment is that the biological oxidation of organic matter will decrease the available substrate for microorganism regrowth in the distribution system and decrease the amount of precursor available to form disinfectant by-products. Organic compounds can support microbial growth in the treatment processes and ammonia, iron and manganese are also suitable for growth for certain bacteria. Bacterial slimes in the distribution systems may lead to corrosion of pipes and taste, odor and colour problems in finished water (Huck and Rittmann 1989).

It has been recognized for some time that microbial activity on granular activated carbon (GAC) is a natural consequence of treating water that contains biodegradable organics, and can be used as a method of water treatment (AWWA Committee, 1981). Therefore, the means to achieve biological treatment is to accumulate an adequate mass of microorganisms which carryout the necessary reactions. Microorganisms utilize substrate for growth and maintenance. Therefore improving the water quality requires an electron donor, electron acceptor and nutrients. Huck and Rittmann (1989) explained that an electron donor is a chemically reduced compound that can be oxidized through microbially catalyzed reactions. The oxidation reaction provides an electron which microorganisms use to reduce the nutrient for cell synthesis and maintenance. An electron acceptor is a chemically oxidized compound that can be reduced through catalyzed reactions. The nutrients are building blocks for cell mass and include carbon, nitrogen, phosphorous, sulphur and oxygen.

It is desired to have biodegradable organic matter (BOM) to enhance the microbial activity which occurs on the filter media. Ozone as a pre-oxidant is the strongest water treatment oxidant available, therefore compounds which may be resistant to oxidation have a better chance of being oxidized by ozone. The organic by-products of ozone are more susceptible to aerobic biodegradation than are those of chlorination. Preozonation converts some larger less biodegradable organics into smaller more biodegradable fractions. The extent of conversion depends on ease of oxidation of specific organics present and on amount of ozone present.

2.1.1 Biofilm Kinetics

Biofilms are aggregates of microorganisms attached to a surface. In the treatment process, attachment and accumulation as a biofilm is a productive mode of biomass retention and results in accumulation of large masses of organisms growing at a slow rate. The concentrations of growth supporting substrate are low in most water supplies, therefore the key to successful biological attachment is the potential to support a high specific growth rate and have efficient retention of biofilm (Rittmann, 1990).

There have been numerous biofilm methods presented in the literature. The theoretical basis for biofilm kinetic modeling has been well documented in the wastewater literature. Numerous complex biofilm models have been found in the literature (Williamson and McCarty, 1976a,b; Rittmann and McCarty, 1980; Suidan and Wang, 1885; Bouwer and Cobb, 1987; Characklis and Marshall, 1990; Saéz and Rittmann, 1992; Billen et al., 1992 and Gujer and Wanner, 1990). A simple design and analytical method presented by Heath et al. 1990, gives a simplistic approach in understanding Biofilm models. More recently, Zhang and Huck (1993a,b) have applied a pseudo analytical solution to the analysis of pilot plant AOC data.

Figure 1 illustrates the idealized biofilm. Although numerous publications have supplied the mathematics for kinetic modeling, three critical aspects of biofilm kinetics are described below: 1) mass transport to the biofilm, 2) diffusion within the biofilm and 3) utilization kinetics within the biofilm.

Rittmann and Huck, (1989) describe that the substrate concentration is not necessarily the same for all microorganisms in the biofilm since reactions and diffusion occur together within the biofilm. The reaction is the utilization of a substrate and its rate is proportional to the concentration of the substrate. The substrate in the bulk liquid must first be transported across the biofilm/liquid interface and then through the biofilm. This transport is by molecular diffusion. Therefore, Figure 1 indicates that substrate utilization lowers the substrate concentration in the biofilm and creates a driving force for diffusion of substrate in the film. In order to model the biofilm kinetics, the flux (J) of a substrate into the surface of the biofilm needs to be predicted. Since reaction with diffusion creates non-uniform concentrations in the biofilm, the solution of the model is to have J as a function of substrate concentration at the surface of the biofilm, S_S. This requires numerical solution techniques.

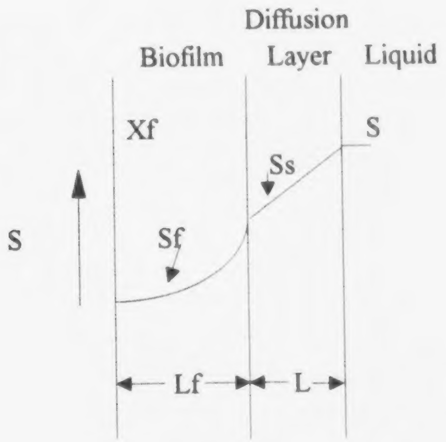

Figure 1: An Idealized Biofilm (after Rittmann and Huck, 1989)

Another important aspect of biofilm kinetics is the mass-transport resistance to the biofilm/liquid surface. Figure 1 illustrates the usual representation of external mass-transport kinetics, showing that the substrate concentration decreases from S to S_S across the effective diffusion layer of depth, L. Therefore, the concentration at the surface of the biofilm usually is lower than the measured bulk concentration. Rittmann and Huck (1989), states that having the external mass transport coupled in series to reaction with diffusion in the biofilm significantly increases the modeling complexity.

The final important feature of the biofilm is the distinction between steady state and non-steady-state. A steady-state biofilm is one for which the growth of new biofilm mass from substrate utilization is balanced by losses of biofilm mass, primarily from maintenance respiration and detachment. (Rittmann and McCarty, 1980). Therefore, the amount of attached biomass and the thickness of the biofilm remains constant. A key feature of the steady-state biofilm is the existence of a minimum substrate concentration that allows growth and maintenance of a steady-state biofilm. The minimum concentration, S_{min}, is defined mathematically as:

$$S_{min} = \frac{b'K_s}{Yk - b'}$$

Where:

S_{min} = minimum allowable concentration of the rate limiting substrate for steady state biofilm, milligrams per liter

K_s = Substrate concentration at which rate is half the maximum (Monod Kinetics), milligrams per liter

Y = true yield coefficient, milligram cells per milligram

b' = total biofilm loss rate coefficient, liter per day.

k = the maximum specific rate of substrate utilization, milligram cells per liter

For concentrations less than S_{min}, the biofilm has a net loss and it is therefore impossible to sustain a steady state biofilm when $S < S_{min}$. Any situation which does not meet the definition of a steady-state biofilm has a non steady-state biofilm. Although for $S<S_{min}$ theoretically a steady state biofilm could not be supported, in reality some small microbial population may exist and therefore would use substrate at a very slow rate if substrate was still present. It is also recognized that the microbioal population may be different along the length of a contactor.

2.1.2 Measurement of Biodegradable Organic Matter (BOM)

Total organic carbon (TOC) concentration ranges from 0.1 to 2 mg/L in groundwater and 1 to 20 mg/L in surface water (Bouwer and Crowe, 1988). TOC is generally comprised of natural organic matter (NOM) derived from living and decaying vegetation. A significant proportion of NOM is generally referred to as humic substances which consists of complex polyaromatic compounds of high molecular weight. A small fraction of TOC is comprised of synthetic organic compounds (SOC's). These compound appear in lakes, rivers and groundwater from the misuse of industrial, municipal, urban and rural discharge practices (Bouwer and Crowe, 1988).

Of particular interest is the amount of biodegradable organic material (BOM) present in the water supply. Biodegradable organic carbon (BDOC) is that portion of the organic carbon in water that can be mineralized by heterotrophic microorganisms. Assimilable organic carbon (AOC) is that portion of the biodegradable organic carbon that can be converted to cell mass and can be expressed as a carbon concentration by means of a conversion factor or calibration (Huck, 1990). The test procedure for AOC usually measures easily biodegradable material.

The AOC measurement is a biomass-based method, and is based on BOM being the limiting nutrient for growth. The AOC methods can be divided into two major groups on the basis of the inoculum used; either one or several known organisms, or the indigenous bacteria from the water being tested. The van der Kooij, (1982) AOC technique is most commonly employed. This method uses two bacterial strains, *Pseudomonas fluorescens* strain P17 and *Spirillum* strain NOX (van der Kooij, 1987, 1989 and 1990). The results are expressed as acetate carbon equivalents or oxalate carbon equivalents.

The BDOC measurement is a DOC based method, which measures a difference in DOC before and after sample incubation (Δ DOC). Typically the DOC-based methods require much less sample manipulation than the methods requiring the determination of colony forming units (biomass-based). Although the Δ DOC methods are less labor-intensive, they do require a good low-level TOC analyzer. In addition all of the methods require a good technique for cleaning glassware in order to avoid contamination. Neither the biomass-based nor the DOC based approaches are inherently faster. Both these approaches offer a procedure that can be completed in a few days. Measurement of BOM below approximately 0.2 mg/L typically requires a biomass-based approach to achieve sufficient sensitivity. Huck (1990) notes that the AOC value obtained with the van der Kooij method may be only a small fraction of the total organic carbon (TOC) and may be considerably lower than values obtained with other methods. Therefore if AOC were to be an operational parameter the results would need to be interpreted accordingly.

It is important to note that the biomass and DOC based assay measure a different parameter. The two parameters are related and use of both types of assays will provide complementary information. Huck (1990) provides a description of the known measurement techniques available to determine AOC and BDOC and provides a critical review of these methods. The methods used to determine these parameters in this study are described in detail in Section 3.0.

2.2 Performance of Biological Drinking Water Treatment

Numerous pilot and full scale water treatment studies have been conducted and their results presented in the literature. The performance of these studies have been generally reported as 1) removal of biodegradable organic matter (BOM) which include natural organic matter (NOM), synthetic organic compounds (SOCs), and specific measures for BOM (AOC and BDOC), 2) removal of chlorinated by-products and 3) removal of ozonated by-products. The following sections provide a detailed review of a number of these studies.

2.2.1 Removal of Biodegradable Organic Matter (BOM)

Earlier studies investigating the removal of organic matter were often only monitored using the measurement of total organic carbon (TOC). A study by Maloney et al.(1984) reported that TOC removal occurred on all contactors or filters, used in their study. TOC efficiency was greater for GAC contactors than sand filters and a general increase in removal efficiency was noted when warm influent water was used. A different study conducted by Glaze and Wallace (1984) reported TOC removal for GAC contactors in series. They reported that TOC removal was about 50 percent, and only slightly better removal was obtained for pre-ozonated water. A more recent study in Edmonton (Huck et. al, 1991a) reported an average overall TOC removal of 65 percent from the raw water, where dual media filtration and GAC contactors were used. The removal percent included significant removal during sedimentation. Although the measurement of TOC provides a good measure of the removal of organic carbon in the treatment process, it is more desirable to monitor the amount of biodegradable carbon removed.

A considerable amount of effort has been devoted to investigating the removal of specific organic compounds through the use of biological treatment. Phenol has been shown to be relatively adsorbable and biodegradable, and has been used in several investigations involving degradation at low substrate concentrations (Subba-Roa et al, 1982; Wiggins et al, 1985; Chesney et al., 1885; Shimp and Pfaender, 1985b; and Jones and Alexander, 1986). DeWaters and DiGiano (1990) investigated the removal of phenol in the presence of NOM in a GAC contactor. It was found that ozonation encouraged biofilm growth and biodegradation of NOM, and readily degraded trace concentrations of phenol. A similar result was found by Speitel et al (1989), in a study where the removal of

2,4,dichlorophenol (DCP) was also investigated. They reported that the degradation of DCP was negligible even in the presence of ozonation.

The removal of SOCs in the presence of other strong oxidants or in combination with ozone has also been well documented (e.g. Duguet et al., 1989, and Dewaters and DiGiano, 1990). One such study by Duguet et al (1989) reported that the reduction of chloronitrobenzenes from 1990 μg/L to less than 20 μg/L could be reached by the application of 8 mg O_3/L and 3 mg H_2O_2/L with a 20 minute contact time. Similar results were reported for benzoic compounds when both sands filters and GAC contactors were used.

The measurement of biodegradable organic carbon (BDOC) is frequently used to report the removal of dissolved organic carbon (DOC). Recently Servais et al (1992) reported the impact of empty-bed contact time and temperature on the efficiency of biological GAC filtration for pilot filters at the Neuilly-sur Marne treatment plant in the suburbs of Paris, France. They reported that with a fixed bacterial carbon biomass of 2 mg/L, pilots with an EBCT of 10 minutes could achieve 60 percent removal of BDOC. They also reported that BDOC removal increased with increasing EBCT in a tested range of filtration velocities (6-18 m/h). Comparable results have also been found from a study at a water treatment plant in Ivry-sur-Seine near Paris by Bonnet et al (1992). The treatment consisted of a preozonzation treatment, contact coagulation, coagulation, slow sand filtration, ozonation and GAC filtration. They reported that measurement of BDOC was a "sure" technique which would give low levels of BDOC preventing bacterial aftergrowth. More currently, research by Carlson and DiGiano (1992) tested a bio-reactor to assist in determining the treatability of water by BAC. They found that nutrient addition was not needed to remove BDOC in the bio-reactor, and that little gain in BDOC removal was found by dosing ozone in stages.

The most commonly reported BOM parameter is AOC. The removal of this form of carbon is of particular interest to the water treatment industry because the amount of AOC reaching the distribution system influences the amount of microbial growth therein (Huck, 1990).

AOC levels have been shown to increase following ozonation, and to be reduced after sand and GAC filters (e.g. van der Kooij et al, 1882; Janssens et al, 1984). A recent study by Reasoner et al (1992) reported that the single species (P17) AOC bioassay indicated that ozonation resulted in a minimum increase in AOC and after filtration the AOC value decreased. However, the dual species (P17 + NOX) AOC bioassay results, although limited, indicated that the total AOC tended to increase from the ozonation step to the finished water. They suggested that the dual media filters contributed some AOC to the finished water.

Huck et al (1991) presented data from an Edmonton pilot plant study showing that raw water AOC varied seasonally, and AOC removal was achieved after coagulation, flocculation, and sedimentation. It was also reported that ozonation produced both an increase and decrease in AOC with an effluent AOC of 50 μg/L being met 90 percent of the time by the dual media filters followed by GAC contactors.

A study at a Laval, Québec biological treatment plant by Prévost et al (1989) noted that biological removal of AOC was maintained even if cold water temperatures (1-5^{O}C) were experienced for an extended period. They also reported that removal of more than 80 percent of AOC required longer EBCT in cold water than in warm water. A study by LeChevallier et al (1992) also noted that an AOC removal of 80 percent could be achieved even at low temperatures. They also applied free chlorine to GAC filters and found that it did not inhibit AOC removal. The free chlorine would have been removed by reaction in the GAC contactors, therefore not inhibiting AOC removal. They reported that prechlorination resulted in significantly lower effluent AOC levels than did preozonation. In contrast, Miltner and Summers (1992) reported that AOC-NOX generally increased in a chlorinated filter and control of AOC-NOX by biodegradation was generally better in non-chlorinated filters.

In summary TOC and some SOC's have been shown to be successfully removed through biological treatment, and enhanced removal has been achieved in the presence of preozonation. However, these parameters are not a true measurement of the biodegradable organic carbon being removed by the treatment. The measurement of BDOC and AOC are more desirable parameters to monitor, since removal efficiencies indicate the biological instability of the finished water. BDOC has been consistently shown to be significantly reduced through biological treatment The measure of AOC has shown varying results in removal trends, however typically AOC is a) reduced through coagulation, flocculation and sedimentation, b) increased after ozonation and c) decreased after sand and GAC filtration. The role of chlorine as pre-oxidant appears to be unclear in enhancing biological treatment.

2.2.2 Removal of Chlorinated By-Product Precursors

Many organic components of natural waters have been shown to be associated with the formation of halogenated organic by-products. They include humic and fulvic matter, algal-derived organic matter, amino acids, and aromatic-ring compounds. Several groups of chlorine disinfection by-products have been identified, including the trihalomethanes (THMs), haloacetonitriles (HANs), and haloacetic acids (HAAs). Other specific compounds often analyzed for are chloral hydrate (CH), 1,1,1,-trichloropropanone (111-TCP), cyanogen chloride (CNCl), and chloropicrin (CP). Collectively, chlorinated organic substances are measured as Total Organic Halogen (TOX) or Absorbable Organic Halogen (AOXFP). Chlorine demand, which measures the amount of chlorine consumed under specified conditions, is another measure of the amount of reactive organic material present.

Numerous studies have investigated the removal of chlorinated compounds through the used of biological treatment. One such study in France (Bourbigot et al, 1986) concluded that a combined treatment of ozone and activated carbon decreased the chlorine consumption of treated water and consequently reduced the formation of chlorinated organic compounds. Since these studies more emphasis has been placed on the removal of specific groups of chlorinated compounds such as THM)s. More recently Chang and Singer (1991) reported that from investigating waters from seven utilities which used ozone as a preoxidant, it was found that preozonation lowered the THM Formation Potential (THMFP) by about 10 percent at dosages commonly used in practice.

A significant relationship between TOC and THMFP has been reported by many investigators. LeChevallier et al (1992) indicated that TOC levels <2 mg/L could be related to THMFP of <100 μg/L. They also reported that biologically active GAC-sand filtration (10-min EBCT) could produce a steady-state reduction in THMFP of 54 percent over a one-year period. This study also evaluated chlorine disinfection by-products from both pre-ozonated and pre-chlorinated streams. As expected, THMs, TOX, HANs, CH and total haloketones were higher in the prechlorinated system than in the ozonated system.

Huck et al (1991a) reported that except for the ozonation step, THMFP, and TOXFP were correlated with AOC (measured by the van der Kooij method) at different points in a pilot-scale biological treatment process. They also noted that a generally good correlation between AOC values and chlorine demand in the treatment train was found. Excellent removal was reported for TOXFP and chlorine demand, where 78 and 72 percent of raw water concentrations were removed for TOXFP and chlorine demand respectively.

More recent studies reported by Miltner and Summers (1992) and Reckhow et al (1992) have also investigated the removal of chlorine disinfection by-products. Miltner and Summers (1992) concluded that the biodegradability of chlorinated by-product precursors decreased in the order: HAA > THM > TOX. Reckhow et al (1992) stated that the removal of DOC, THM precursors and HAA precursors reflected general removal of natural organic matter, which is largely attributed to physical and chemical effects.

Another disinfection by-product of concern due to its carcinogenicity, is chloral hydrate (trichloroacetaldehyde hydrate). A recent study by Xie and Reckhow (1992) noted that preozonation enhanced the formation of chloral hydrate. However, a moderate amount of chloral hydrate precursor was removed by anthracite/sand filtration, and bioactive GAC filters resulted in a significant reduction of chloral hydrate precursors.

In summary the removals of chlorine disinfection by-products are qualitatively, and in some cases quantitatively, related to the removal of BOM. Increased removals are favored by the use of pre-ozonation, low filtration rates (high EBCTs), the absence of chlorine as a pre-oxidant or residual in backwash water, and the used of GAC instead of anthracite. These characteristics in a treatment facility offer better removal of chlorinated by-product precursors; however, specific removal depends on raw water characteristics and specific operating conditions.

2.2.3 Removal of Ozonation By-Products

The use of ozone in water treatment unquestionably results in the formation of by-products. From studies available it seems that, at typical doses used in current water treatment practices, ozone produces a variety of by-products which are formed at different stages of oxidation. Despite the increasing application of ozone in water treatment, there is limited information available on by-products of ozonation. Recent advances in the trace-level analysis of low molecular weight aldehydes in water (Glaze et al, 1989) have led to increased monitoring of this important class of ozonation by-products.

Glaze et al. (1989) analyzed two surface waters in Southern California for ozonation by-products. Their findings showed that the major neutral by-products were the aliphatic aldehydes, but levels varied between water source despite the similar water treatment. They also reported lower levels of other compounds found in the ozonated water including bromoform and possibly ketones. More recently, a study by Weinberg and Glaze (1992) drew several important conclusions from several plants surveyed. They concluded that 1) aldehydes and aldo-ketones are ubiquitous ozone DBPs formed in all treatment plants studied, 2) hydrogen peroxide was formed in all ozonation processes and is accompanied by unidentified organic hydroperoxides, 3) aldo and ketoacids, previously unreported in treatment plants, are formed along with aldehydes but at lower levels, 4) bromate is formed when bromide is present in raw waters and appears to be a function of the ozone residual and bromide levels, 5) With the exception of bromate, other by-products are removed by filters which possess an active biomass, and 6) post disinfection with chlorine or chlorine dioxide also appears to form aldehydes and peroxides which persist in the distribution system.

Recently pilot scale studies have reported trends in the formation of ozonation by-products. Huck et al. (1990) showed that formaldehyde was well removed in biological treatment whereas acetaldehyde was not. Miltner (1992) reported that upon ozonation, mean formaldehyde concentrations reached 26.3 μg/L. Concentrations subsequently declined through conventional treatment but were elevated again upon chlorination. He noted similar behavior with acetone and glyoxal. Additional studies by Miltner and Summers (1992) and Miltner et al (1992) showed that aldehydes and ketones are biodegradable. The bacteria apparently utilize the aldehydes and ketones as nutrients.

A study by Reasoner et al (1992) noted that ozonation resulted in an increase in the concentration of aldehydes in the water, particularly formaldehyde and acetaldehyde. They suggested that these and other compounds resulting from the oxidation of organic compounds by ozone contribute to the total AOC available for microbiological growth. However, results from a full scale study by Reckhow et al (1992) more conclusively demonstrated that removal of AOC, aldehydes and keto-acids simply reflects biodegradation of oxidation by-products of NOM. In addition it was proposed that aldehydes and keto-acids may have utility as model biodegradable compounds indicating the level of biological activity in a water treatment system.

Krasner et al (1992) conducted a study comparing the removal of AOC and aldehydes. They suggested that aldehydes may act as a surrogate for AOC data and unknown ozone by-products. It was also interesting to note that effective removals were obtained for shorter than normal EBCTs.

In summary, a number of ozonation by-products have been identified and analytical methods have been successful in quantifying these major compounds. Biological treatment has been shown to effectively remove most of these known by-products, however, chlorination of final effluents typically increases the concentration of these compounds.

2.2.4 Relationships for Removal of BOM and Related Parameters

As discussed previously, the theoretical basis for biofilm kinetic modeling has been well documented in the wastewater literature, and many complex biofilm models have been developed. However the solution of these models is mathematically or computationally complex and requires a detailed understanding of the various parameters impacting the biological processes taking place in water treatment. The application of these models to drinking water treatment is only now being attempted (Huck, 1993).

An empirical modeling approach has been proposed by Huck and Anderson (1992), who first noted that the removal rate of NVOC, chlorine demand, and AOXFP was directly proportional to the influent concentration of these parameters. It was found that a single first-order rate constant could be used to describe the removal process. Their findings showed that in dual media filters, the rate constants were higher for AOXFP, and for chlorine demand following a higher ozone dose. In the GAC contactors, the rate constant was approximately the same for all parameters.

Further investigation was completed by Huck et al (1993), where data from two pilot scale studies and one full scale investigation were analyzed. Parameters analyzed were; BOM (AOC and BDOC), chlorine demand, THMFP and AOXFP. They found that apparent first order rate constants for all parameters fell in a relatively narrow range. It was identified that a more sophisticated modeling approach may be required for AOC because of a wider variation in rate constant; however for other parameters, the simple first order relationship developed could be very useful.

The writer was unaware of any other attempts to provide a quantitative framework to interpret the data obtained in biological drinking water treatment investigations.

2.2.5 Identification of Research Need

The above studies show the need and potential for the development of an extremely useful modeling method to describe the removal of BOM, chlorination by-product precursors and possibly ozonation by-products. There is a need for a simple relationship to predict removal efficiencies and to perform preliminary design. Such a relationship would also be helpful to plan confirmatory pilot studies and to provide a framework for more sophisticated modeling. The first-order relationship needs to be applied to a variety of water types as well as to ozonation by-products and additional chlorinated by-product precursors to determine the range of its applicability. There also needs to be consideration of the effect of operating conditions, specifically water temperature, ozone residuals, filter media and empty bed contact time.

The objective of the research described in this thesis was to conduct such an evaluation. Raw data was collected from six different biological water treatment studies for a wide range of parameters. Details of the data analysis are provided in the following sections. The results of the analysis are discussed and compared, pointing out when different operating conditions and experimental methods were employed. The final task completed indicated how this modeling technique can be easily applied to estimate removal efficiencies for various parameters, in addition to determining the limiting parameter for a specific design application. The limitations to this empirical modeling technique will be identified and recommendations to enhance its usefulness will be made.

CHAPTER 3
ANALYTICAL METHOD

This chapter provides a description of the analytical methods used for all the major classes of compounds which were analyzed during the Edmonton, Alberta 1992-1993 study. In most cases the parameters reported in the other pilot studies used the same or similar analytical methods, however if a different analytical procedure was employed it will be mentioned during the discussion of the particular parameter in Chapter 5. All methods used for the analysis of these compounds are either referenced in recent papers or are standard methods (EPA, APHA-AWWA-WPCF) or are adapted from methods frequently used. The specific method used for each group of compounds is indicated in the following sections.

The author's role in the 1992-93 Edmonton study was to refurbish and operate the pilot plant, and perform sampling and project co-ordination activities. The actual sample analyses were carried out by others. The data from the other studies was obtained from the researchers who conducted the investigations.

Non-Volatile Organic Carbon (NVOC)

NVOC samples were collected in 500-mL glass bottles and sealed with PTFE-lined caps (APHA-AWWA-WPCF, 1989). Shortly after collection the samples were acidified to pH 2 with sulfuric acid. The samples were analyzed routinely within hours of collection and stored in the dark at 4 °C if this was not possible. Before the analysis, the samples were purged twice for a total of 8-10 min with purified oxygen (zero gas) to remove most of the inorganic carbon. The analyses were performed in triplicate with a total organic carbon analyzer[1] utilizing ultraviolet (UV)-promoted persulfate oxidation followed by infrared (IR) detection of the resulting carbon dioxide. The samples were analyzed for total carbon and inorganic carbon, and the difference between these values resulted in NVOC. The NVOC is referred to as TOC in some of the other studies mentioned in Chapter 5.

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[1] Dohrmann DC-80, Xertex Corp., Santa Clara,Calif.

Assimilable Organic Carbon (AOC)

AOC determinations were completed using the method described by van der Kooij et al (1982), with some modifications described by Huck et al. (1991). The 600 mL samples were collected in flasks and heated in a 90°C water bath for 5 min to facilitate a rapid rise to 60 °C and destroy vegetative cells. The samples were then transferred to a 60°C oven for 60 min. The samples were cooled to room temperature in an ice bath and seeded to a concentration of 25 to 250 cfu/mL with each strain (P17 and NOX) simultaneously.

Triplicate spread plates were inoculated on agar[2] with water samples from each flask. The plates were then incubated at 28° C for 48 hours, and colonies were counted. The flasks containing the water samples were incubated at 15°C, and spread plates were prepared approximately every two to three days until a maximum number of colony forming units (N_{max}) was obtained. The yields established by the laboratory for the Edmonton, Alberta 1992-1993 study for *P. fluorescens* strain P17 and *Spirillum* strain NOX were 2.2×10^6 and 1.1×10^7 cfu/µg acetate C, respectively. These show good agreement with published values 4.1×10^6 and 1.2×10^7 cfu/µg acetate C (van der Kooij, 1987).

Several difficulties were identified by Huck et al (1990). Their conclusions are as follows: The lack of survival of the P17 strain following sedimentation were attributed to the use of polyaluminum chloride as a coagulant. This effect was not evident at low doses. Incidents of inhibition of P17 following ozonation have been observed but not explained.

Biodegradable Organic Carbon (BDOC)

The procedure followed for biodegradable organic carbon is that described by Servais et al. (1989) and Block et al. (1992). The experimental protocol is as follows. A 200 mL water sample was sterilized by filtration through a 0.2 µm-pore size membrane (Nuclepore membrane or cellulose acetate Sartorius membrane) which had been carefully rinsed first with distilled water and then with the water sample. A 2-mL inoculum containing autochthonous bacteria was added. In the case of ozonated or chlorinated water, sodium trisulfate was added to neutralize the oxidant excess before the inoculum was added. Incubation of the inoculated samples was performed at 20 ± 0.5 °C in the dark for 4 weeks. Replicated 20 mL subsamples were frozen in sealed glass ampoules in the presence of sodium azide. DOC was measured on a Dohrman 80 Total Carbon Analyzer using UV-promoted persulfate oxidation of organic carbon, and the amount of CO_2 produced was determined by infrared spectrometry. Two DOC determinations were performed on each subsample. The BDOC value was calculated as the difference between the mean values of the initial and final DOC. Although BDOC analyses were initiated in early May 1993 in the Edmonton study, data were not available for inclusion in this thesis. The procedure described in essentially that used in the other studies where BDOC was measured.

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[2] Lab Lemco, Oxoid Canada Inc., Nepean, Ont

Haloacetic Acid Formation Potential (HAAFP)

Several different analytical methods could be used to determined the haloacetic acid formation potential. The method chosen was one by Krasner et al. (1988, 1989) with several modifications. The experimental protocol used is described as follows: A 20-mL aliquot of sample was transferred to a 40 -mL extraction vial. Each vial contained 65 mg of NH_4Cl, (to preserve the sample), 6 g Na_2SO_4, 1.5 mL concentrated H_2SO_4 and 5 mL of 100 µg/L MTBE+DBP (methyl t-butyl ether + 2,3-dibromoproponoic acid). The vials were mechanically shaken for 10 minutes, then allowed 15 minutes to obtain phase separation. Next, the ether layer was transferred using pasteur pipets to a graduated vial half-filled with Na_2SO_4, and 250 µL of CH_2N_2 (Diazomethane). The vials were capped and gently mixed. The samples were esterified for 1 hour at 4 °C in an explosion-proof refrigerator. The extracts were allowed to come to room temperature and then transferred to GC auto sampler vials. A set of calibration-standard extracts was analyzed using the auto sampler. A calibration curve was constructed using a point-to-point fit passing through zero. An internal standard method using a specific internal standard was used to determine unknown concentrations using the fitted curve. In the Edmonton study, the GC operating conditions are given in Appendix A, Table A-12.

Trihalomethanes Formation Potential (THMFP)

The analytical method originally chosen for this parameter was the purge and trap method, however, during the first two months of the project several problems were encountered and it was decided to switch to the pentane extraction method described by USEPA, (1979) and more recently by Koch (1988). The experimental protocol is described as follows. A 20 mL aliquot of sample was withdrawn from the sample container and delivered to a 30 mL vial. A 4-mL volume of pentane containing the internal standard was added by a volumetric dispenser. After all the vials were filled, 5 grams of sodium sulfate plus ascorbic acid (to preserve the sample) was added to each vial. The vials were capped and mechanically shaken for 10 minutes. The vials were removed and allowed to stand for 15 minutes. The extracts were transferred into auto sampler vials by pasteur pipets containing Na_2SO_4. Stock standards were prepared and a calibration curve was analyzed using a GC. The calibration curve was constructed using a point to point fit passing through zero. In the Edmonton study, the GC operating conditions are given in Appendix A, Table A-13.

Total Organic Halogen Formation Potential (TOXFP)

Organic halogens adsorbed to activated carbon were measured according to the draft I.S.O. Method 9562 (1988). This method required a 100 mL aliquot of sample, delivered to a 250 mL flask. Next, 5 mL of nitrate stock solution was added to reduce the pH to less than 2 and 50 mg of activated carbon was also added to the flask. The flask was then shaken in a circular motion for 24 hours at room temperature. The samples were filtered through a 0.45 µm (ϕ 25 mm) polycarbonate filter and analyzed using a EUROGLAS BV Microcoulometric Organic Halogen Analyzer.

Chlorine Demand (CD)

Samples were collected and buffered to pH 7.0 with phosphate buffer. Using NVOC values which had been determined separately for these samples, were then dosed at a 3:1 Cl_2 : NVOC molar ratio with sodium hypochlorite and stored in the dark at 4°C for 7 days. The samples were analyzed for residual chlorine immediately following the 7 day incubation period, based on Standard Method (408,(APHA-AWWA-WPCP, 1989)).

Chloral Hydrate Formation Potential (CHFP)

The determination of chloral hydrate was according to a method described by Krasner (1989). The experimental protocol is described as follows: A 20-mL aliquot was taken from the sample and delivered to a 30 mL extraction vial. A 4-mL aliquot of solvent (methyl t-butyl ether) containing an internal standard (1,2-dibromopropane) was added to the vial. In addition 5 g Na_2SO_4 and ascorbic acid (to preserve the sample) were added and the vials were capped. The vials were mechanically shaken for 10 minutes, and then left 15 minutes to allow the phases to separate. The solvent was drawn off with pasteur pipets. The extract was distributed to auto sampler vials with Na_2SO_4. Standards were prepared and analyzed on the GC and a calibration curve was constructed using a point-to point fit passing through zero. Unknown concentrations were determined by an external calibration method. In the Edmonton study, the GC operating conditions are given in Appendix A, Table A-14.

Aldehydes and Dialdehydes

Low molecular weight carbonyl compounds in natural waters were determined at nanomolar levels by derivatization with O-(2,3,4,5,6,7-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA-HCL) using capillary GC/ECD. This method was similar to that employed by Sclimenti et al. (1990). The following is a description of the analytical procedure. A 20-mL aliquot was measured into a 30 mL extraction vial. To this was added 1 mL of a solution of PFBHA (6 mg/mL). The extraction vial was then placed in a water bath capable of maintaining 45 ± 0.5 °C for 1 h and 45 minutes. After the sample was allowed to cool to room temperature for 20 minutes, 100 µL of concentrated H_2SO_4 was added to quench the derivatization reaction. The derivatives were extracted by adding 4 mL of hexane containing the internal standard and shaking the vial for 10 minutes. The hexane extract was transferred to a vial containing 3 mL of 0.2 normal (N) H_2SO_4 solution and shaken for 2 minutes for clean-up purposes. The hexane layer was then transferred to auto sampler vials, each containing 50 mg of Na_2SO_4 for drying the extract. The extracts were analyzed on a GC using standard calibration curves. The compounds analyzed for in this study were acetaldehyde, butanal, formaldehyde, glyoxal, propanal and methyl glyoxal. In the Edmonton study, the GC operating conditions are given in Appendix A, Table A-15.

Oxo Acids

The analytical method employed was similar to that described to Xie and Reckhow (1992). The experimental protocol is as follows: A 20-mL aliquot was measured into a 30 mL extraction vial. To this was added 1 mL of a solution of PFBHA (6 mg/mL). The extraction vial was then placed in a water bath capable of maintaining 45 ± 0.5 °C for 1 h and 45 min. After the sample was allowed to cool to room temperature for 20 minutes, 100 μL of concentrated H_2SO_4 was added to quench the derivatization reaction. The derivatives were extracted by adding 4 mL of MTBE (methyl t-butyl ether) containing the internal standard and shaking the vial for 10 minutes. The MTBE extract was transferred to a vial containing 10 mL of 0.2 normal (N) H_2SO_4 solution plus Na_2SO_4 crystals then shaken for 2 minutes for clean-up purposes. Next, 250 μL of diazomethane was added to the MTBE layer and stored for 1 h at 4 °C, then transferred to auto sampler vials, each containing silica gel. The compounds analyzed for in this study were pyruvic acid, oxaloacetic, ketomalonic and glyoxylic acid. In the Edmonton study, the GC operating conditions are given in Appendix A, Table A-16.

CHAPTER 4
PILOT PLANT DESCRIPTION

This section provides a description of all the pilot plants investigated. In Chapter 5, the emphasis will be placed on results from the Edmonton, Alberta 1992-1993 study since it is the most current and had a design objective to obtain specific data for modeling. A brief description has been provided for all pilot plant studies, in addition to a schematic diagram, and a table outlining specific operational information. Since the author of this thesis was also responsible for a) reburishment activity, b) operation and maintenance, c) water and filter media sampling, and d) conducting all experiments related to operational activities, at the recent Edmonton, Alberta pilot plant, a very detailed description of all components of the pilot plant has been included in Appendix A.

4.1 Edmonton, Alberta 1989-1990

Huck et al (1991) and Milne et al (1990) described the design of a biological water treatment pilot plant in Edmonton, Alberta for a study conducted from 1989 to 1990. Raw water for the pilot plant was obtained from the North Saskatchewan River at the intake to the Rossdale Water Treatment Plant. Figure 2 is a schematic of the pilot plant and Table 1 outlines the operating parameters. All materials in contact with water were made of stainless steel, glass or a fluorocarbon to prevent organic contamination. Raw water flowed to the pilot plant at 45 L/min passing through a screen to remove stones and leaves. A presedimentation tank provided protection from periodic high influent suspended solids levels. For this tank, a blowdown flow of 15 percent of influent flow was maintained. Coagulation was achieved with polyaluminum chloride with a dosage ranging from 20 to 140 mg/L, although use of the higher dose was infrequent. Rapid mixing was accomplished with a variable speed agitator with a detention time of 16 seconds. A three stage tapered flocculation followed with a detention time of 28 minutes. A tapered velocity gradient was achieved with impeller speed of 30, 20, and 12 rpm. Clarification was completed in a sedimentation tank containing 60 ° parallel plates spaced at 50 mm intervals. Following sedimentation, a settled water storage tank served to split the streams, buffer flow variations and provide a relatively constant head for the pumps feeding the ozone contactors.

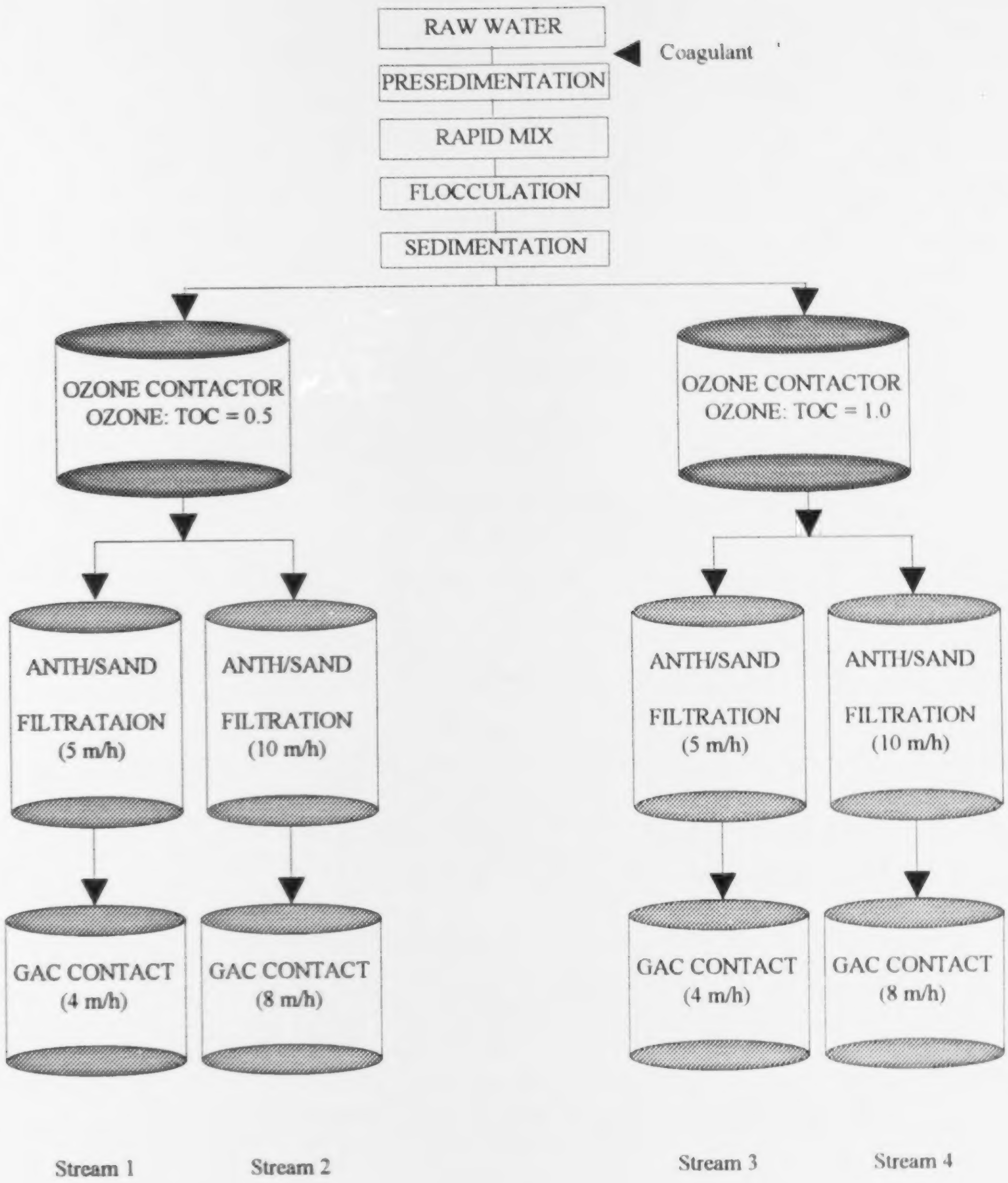

Figure 2: Schematic for the Edmonton, Alberta Pilot Plant, 1989-1990

Table 1:
Operating parameters for Edmonton, Alberta pilot plant, 1989-90 (Huck et al 1991)

Treatment Step	Parameter	Value
Raw water	Flow rate	45 L/min
Screening	Screen opening	3 mm
Presedimentation	Overflow rate	4.8 cm/min
	Detention time	8.3 min
Coagulation	Detention time	16 s
	Polyaluminum Chlorine Dosage	20-140 mg/L
Flocculation	Detention time	28 min (3 units total)
	Velocity gradient	185,40,7/s
Sedimentation	Parallel plates	60 ° inclination
	Plate separation	5 cm
	Detention time	59.4 min
Settled-water storage	Detention time	15 min
Ozonation	Detention time	
	Contactor 1 & 2	10 min
	Applied dose (target)	
	Contactor 1 to filters 1 & 2	0.5 ozone/NVOC
	Contactor 2 to filters 3 & 4	1.0 ozone/NVOC
Filtration	Anthracite depth	450 mm
	Effective size	1 mm
	Sand depth	300 mm
	Effective size	0.4 mm
	Hydraulic loading	
	Columns 1 and 3	5 m/h
	Columns 2 and 4	10 m/h
GAC columns	Carbon	
	Type	GAC[3]
	Effective size	0.55-0.75 mm
	Sieve size	12-14 (US standard)
	Uniformity coefficient	1.9 (maximum)
	Particle density wetted-water	1.3-1.4 g/cc
	Total surface area (N_2 BET)	1050-1200 mm^2/g
	Bed depth	
	Column 1 and 3	2.7 m
	Column 2 and 4	2.8 m
	Empty bed contact time	
	Column 1 and 3	2-40 min
	Column 2 and 4	2-21 min
	Hydraulic Loading	
	Column 1 and 3	4 m/h
	Column 2 and 4	8 m/h

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[3] Filtrasorb 400, Calgon Corp., Pittsburgh, Pa

Settled water was then pumped into one of two ozone contactors operating in a counter current mode. The dose applied to contactors 1 and 2 was 0.5 and 1.0 mg/L ozone per mg/L NVOC respectively. Ozonated water from each contactor was pumped to two of the four anthracite-sand filters. Filtration was carried out in the constant-rate, variable-head mode. Filters 1 and 3 received a hydraulic loading of 5 m/h and Filters 2 and 4 received a hydraulic loading of 10 m/h. Each filter column contained 450 mm anthracite overlying 300 mm sand. The columns were backwashed manually every 24 hours or when the turbidity exceeded 0.5 ntu.

Filtered water was then pumped to the GAC contactors, also operating at a constant rate, variable head mode. Each contactor contained approximately 2.7 m F-400[4] with contactors 1 and 3 receiving a hydraulic loading of 4 m/h and contactors 2 and 4 receiving a hydraulic loading of 8 m/h. The columns provided six sampling ports representing empty bed contact times from 2 to 21 min for the high hydraulic loading and 2 to 40 min at the low hydraulic loading. For each stream, the anthracite-sand filters and GAC contactors were backwashed with stored effluent from that stream.

Sampling for this project was completed approximately every two weeks and more frequently during spring run-off. The North Saskatchewan River exhibits significant seasonal fluctuations in quality, and the most notable usually occur during the spring run-off event which occurs when snow melts in the Rocky Mountains and flows eastward through forested and agricultural area eventually reaching Edmonton. The event brings higher organic loadings to the raw water; the raw water TOC during this study peaked at approximately 11 mg/L. This event is important and required frequent sampling to obtain higher concentrations for all parameters measured. The higher concentrations are required for modeling applications.

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[4] Filtrasorb 400, Calgon Corp., Pittsburgh, Pa

4.2 Woodbridge, Connecticut

The site of this study was the pilot facility at the West River Water Treatment Plant in Woodbridge, CT. The pilot facility comprised a 10 gpm (38 L/min) raw water flow capacity which split into two parallel direct filtration trains. Each of the two trains fed 2-3 dual media filters. The full-scale West River Treatment Plant was an in-line direct filtration facility, employing dual media anthracite-sand filters. A schematic for this pilot plant is displayed in Figure 3. The West River raw water is a low alkalinity (10-15 mg/L $CaCO_3$), low turbidity (≈ 1 NTU), low DOC (≈ 3 mg/L) supply, typical of many New England waters. Specific design parameters are displayed in Table 2.

Table 2:
Operating parameters for Woodbridge, CT pilot plant, (Reckhow et al 1992)

Treatment Step	Parameter	Value
Raw water	Flow rate	38 L/min
Coagulation	Alum Dose	n/a
	Polymer Dosage	n/a
Ozonation	Applied Dose	0.5 - 2.0 mg/L
	Peroxone Dose	1.5 mg/L
	Ozone Residual*	n/a
Filtration	Anthracite depth	508 mm
	Effective size	n/a
	Sand depth	254 mm
	Effective size	n/a
	Hydraulic loading	
	Columns 1 - 5	3.75 - 7.5 m/h
	Empty bed contact time	6.1 - 12.3 min

n/a - not available

* This study employed an O_3 dose plus a peroxide dose, however this thesis only used results from a testing interval which employed O_3.

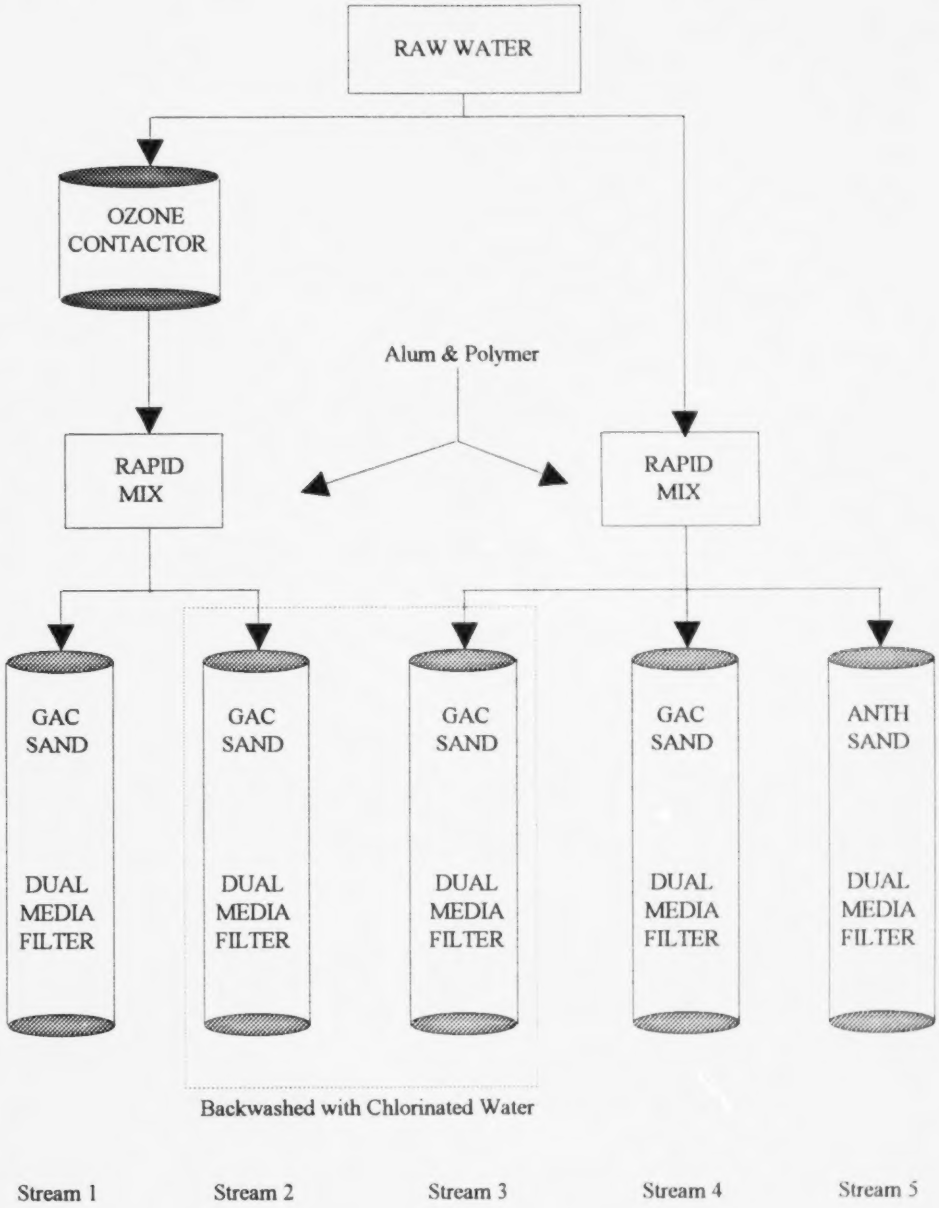

RAW WATER
OZONE CONTACTOR
Alum & Polymer
RAPID MIX
RAPID MIX
GAC SAND DUAL MEDIA FILTER
GAC SAND DUAL MEDIA FILTER
GAC SAND DUAL MEDIA FILTER
GAC SAND DUAL MEDIA FILTER
ANTH SAND DUAL MEDIA FILTER
Backwashed with Chlorinated Water
Stream 1
Stream 2
Stream 3
Stream 4
Stream 5

Figure 3: Schematic for the Woodbridge, CT Pilot Plant

4.3 Southern California

Krasner et al (1992) described a pilot testing study designed to evaluate the biological filtration for the removal of AOC and aldehydes. The pilot testing was divided into two phases. In phase I, six parallel filters were available for preliminary evaluation of filter media and the impact of filtration rate. In phase II, only three filters were available for testing, so emphasis was placed on the evaluation of filter media.

Phase I Testing

Figure 4a displays a schematic of the pilot plant for phase I, and Table 3 outline the operational parameters for this phase. Water from the California State Project (SPW) was ozonated in a 10 ft (3.0 m)deep counter current contactor. An ozone dose (i.e., 1.8 mg/L) sufficient to meet a minimum disinfection criterion (i.e., 0.3-0.4 mg/L) target ozone residual was used. The raw water TOC was approximately 3.5 mg/L; therefore the ozone/TOC ratio would typically be approximately 0.5. The hydraulic residence time in the contactor was 6 min with a water flow of 3.9 gpm (14.8 L/min). The water was typically low in turbidity (≅ 2 ntu) and at this point was split into two parallel trains (not indicated in Figure 4a), and each was coagulated with 5 mg/L alum and 3 mg/L polymer. The flocculation and sedimentation step to follow simulated the full scale operation and had a combined detention time of 2 hours.

The settled water was then spilt and sent to six parallel, 6 inch (150 mm) diameter, glass filters. Three filters contained 20 inches (500 mm) of anthracite coal, over 8 inches (200 mm) of sand. These were operated at 3,6, and 9 gpm/sf. (7.5, 15, and 22,5 m/h) The other filters contained 20 inches (500 mm) of GAC (Filtrasorb-300, or F-300; Calgon Corp., Pittsburgh, PA). In addition to evaluating virgin GAC, used GAC was obtained from GAC capped filters from a conventional treatment plant of the East Bay Municipal Utility District (EBMUD). The GAC from EBMUD had been in service for approximately 3 years and was spent with regard to TOC removal. The spent GAC filters were operated at the maximum and minimum filtration rates under investigation for anthracite. The virgin GAC filter was operated at 9 gpm/sf (22.5 m/h).

Since filtration rates varied from 3 to 9 gpm/sf (7.5 to 22.5 m/h), it was decided to backwash the filters based on the volume of water treated rather than the time of operation. Backwashing was automated such that at filtration rates of 3, 6, and 9 gpm/sf

(7.5, 15, 22.5 m/h) were backwashed every 24, 12, and 8 hours respectively. The pilot-scale filters were backwashed with chlorinated water from the full-scale plant effluent. However, a GAC canister was used to remove most of the chloramine residual (typically down to 0.2 mg/L). The GAC canister was replaced when the residual exceeded 0.4 mg/L. In addition, the filters received a surface wash, using the same water used in backwashing, with a modified Baylis nozzle. The filters were backwashed with a 20 to 30 percent bed expansion.

Phase II Testing

Figure 4b is a schematic of the pilot plant for phase II testing, and Table 3 outlines the operational parameters for this phase. During the phase II testing SPW was not available, so Colorado River Water (CRW) was evaluated. CRW typically had a lower ozone demand and fewer DBP precursors than SPW. Therefore, with a raw TOC of approximately 2.5 mg/L, an ozone dose of 1 mg/L was used to meet a target ozone residual of 0.4 to 0.5 mg/L. This dose corresponded to a ozone/TOC ratio of 0.4. The influent turbidity was typically $\leq$ 1 ntu, and this water was coagulated with 6 mg/L alum and 3 mg/L polymer. In this phase all filters were operated at 6 gpm/sf (15 m/h). The media evaluated were anthracite coal, F-300 GAC and Picabiol© GAC. These filters were backwashed using the same method as in phase I.

Table 3
Operation parameter for the Southern California Pilot Plant (Krasner et al, 1992)

Treatment Step	Parameter	Value
Raw Water	Flow rate	3.9 gpm/sf (14.8 L/min)
Ozonation	Height of Contactor	16 ft (4.9 m)
	Dose	
	Phase I (SPW)	1.8 mg/L (Ozone/TOC=0.5)
	Phase II (CRW)	1.0 mg/L (Ozone/TOC=0.4)
Coagulation	Dose Phase I	
	Alum	5.0 mg/L
	Polymer	3.0 mg/L
	Dose Phase II	
	Alum	6.0 mg/L
	Polymer	3.0 mg/L
Flocculation/Sedimentation	Detention time	2 hours
Filtration	Anthracite depth	20 inches (500 mm)
	Sand depth	8 inches (200 mm)
	GAC depth	20 inches (500 mm)
	Hydraulic flow rate	
	Phase I	
	FE1 and F6	3 gpm/sf (7.5m/h)
	FE3	6 gpm/sf (15 m/h)
	FE2, FE4, and FE5	9 gpm/sf (22.5m/h)
	Phase II	
	FE1, FE3, FE5	6 gpm/sf (15 m/h)

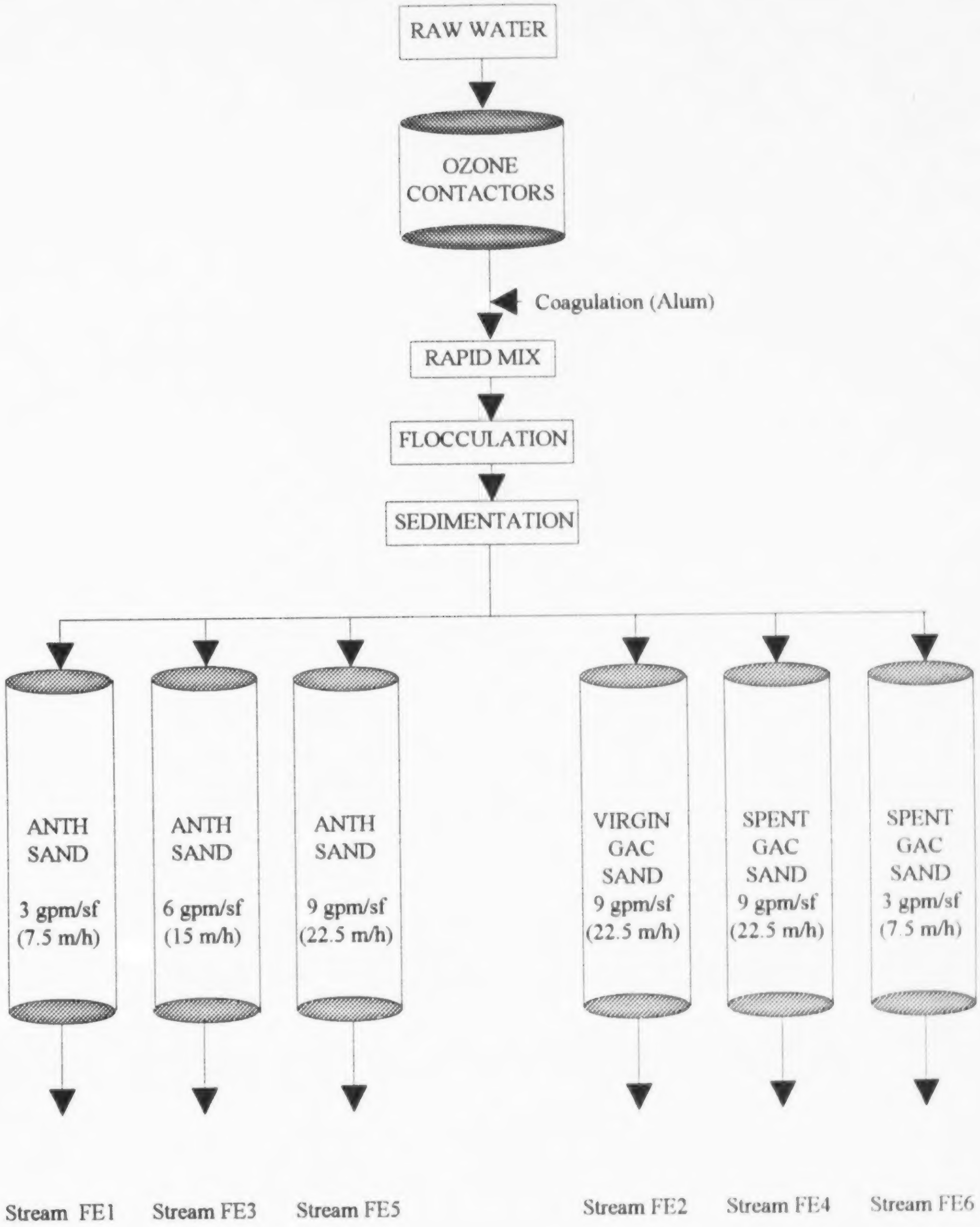

RAW WATER
OZONE CONTACTORS
Coagulation (Alum)
RAPID MIX
FLOCCULATION
SEDIMENTATION
ANTH SAND 3 gpm/sf (7.5 m/h)
ANTH SAND 6 gpm/sf (15 m/h)
ANTH SAND 9 gpm/sf (22.5 m/h)
VIRGIN GAC SAND 9 gpm/sf (22.5 m/h)
SPENT GAC SAND 9 gpm/sf (22.5 m/h)
SPENT GAC SAND 3 gpm/sf (7.5 m/h)
Stream FE1
Stream FE3
Stream FE5
Stream FE2
Stream FE4
Stream FE6

Figure 4a: Schematic for the Southern California Pilot Plant Phase I

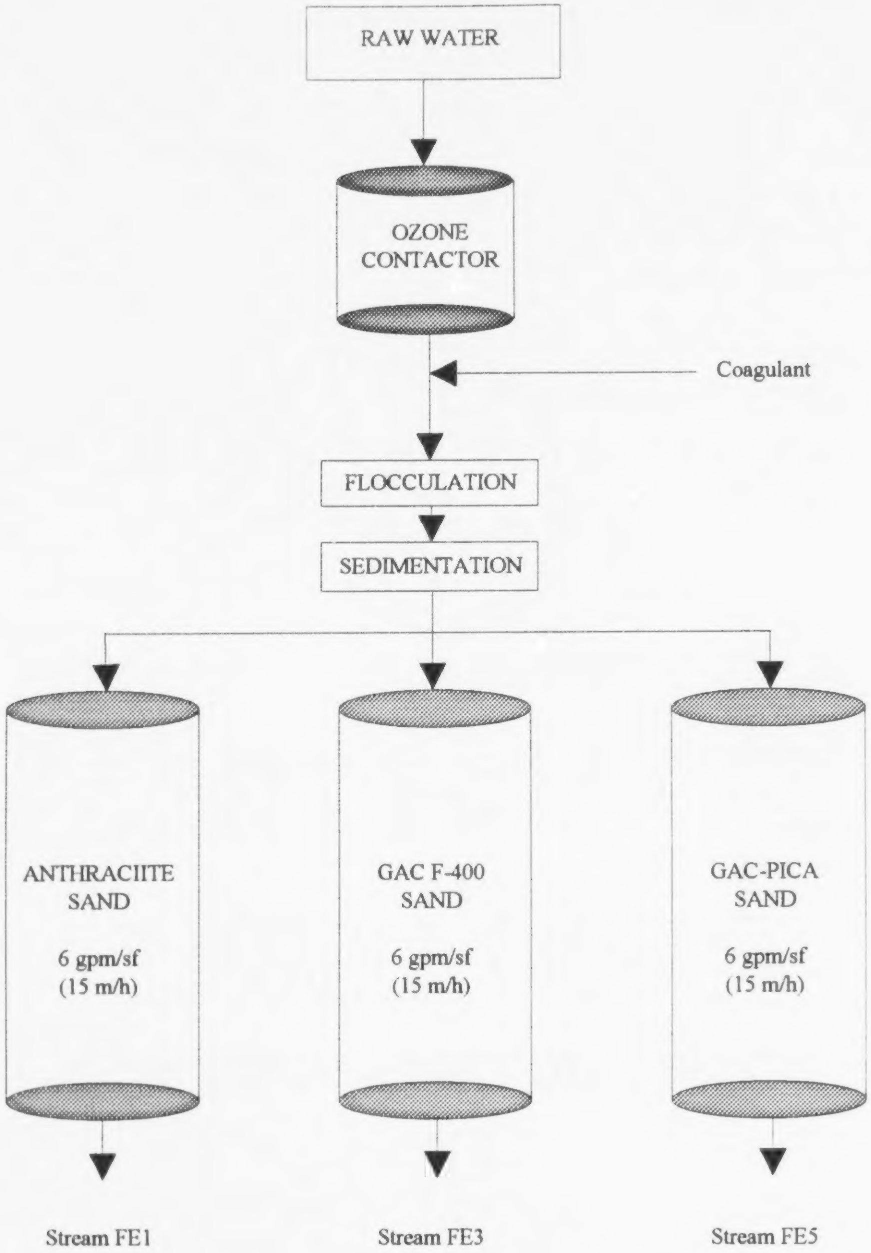


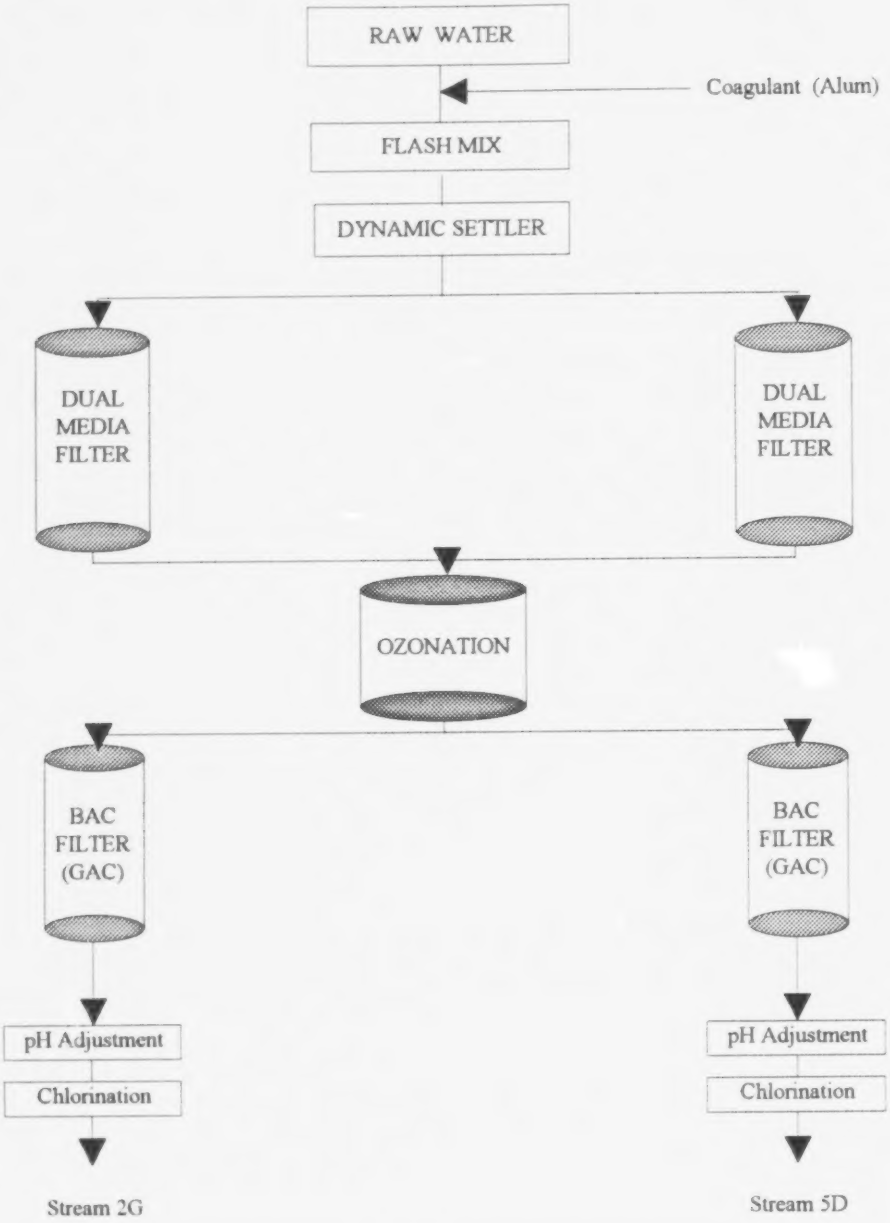
Figure 4b: Schematic for the Southern California Pilot Plant, Phase II

4.4 Laval, Quebec

Water for the pilot plant study was obtained from the Mille-Iles River, which has a high organic loading (5-9 mg/L TOC) and is subjected to strong seasonal variations in temperature (0.5 - 28 °C). This particular study lasted for approximately 1 year and the treatment steps included coagulation, flocculation, sedimentation, dual media filtration, ozonation and BAC filtration. A schematic for this study is displayed in Figure 5. Specific design parameters are given in Table 4. For at least part of this study, the pilot scale coagulation/flocculation/sedimentation step was not in use. Rather, settled water was obtained from the full scale plant, which used the same process.

Table 4
Operation parameter for the Laval, Quebec Pilot Plant (Prévost et al, 1992)

Treatment Step	Parameter	Value
Coagulation	Alum Dose	30-45 mg/L
	Polymer Dose	1.2-2.5 mg/L
Sedimentation	Rate	4 m/h
Filtration	Hydraulic Loading Rate	4-10 m/h
	Anthracite depth	650 mm
	Effective Size	0.8 mm
	Uniformity Coefficient	1.8
	Sand Depth	150 mm
	Effective Size	0.4 mm
	Uniformity Coefficient	1.5
Ozonation	Ozone Dosage	1.5 mg/L
	Contact Time	8 minutes
	Ozone Residual	0.4 mg/L after 4 min
BAC Filtration	GAC type	F-400
	Effective Size	0.63 mm
	Uniformity Coefficient	1.65
	Density	0.43 g/cm^3
	Bed Depth	2.0 m
	Hydraulic Loading Rate	4-10 m/h
Post Filtration	pH adjustment	20 mg/L $CaCO_3$
Disinfection	ClO_2 Dose	0.2 - 1.0 mg/L
	Contact Time	6-12 h



** note that seven BAC filters exist, however only data for the above filters was provided

Figure 5: Schematic for the Laval, Quebec Pilot Plant

4.5 Cincinnati, Ohio

Miltner and Summers (1992) described a biological treatment study conducted by the USEPA's Drinking Water Research Division in conjunction with the University of Cincinnati. The pilot plant employed preozonation and parallel biological filters. Raw Ohio River water was trucked from the Cincinnati Water Works to the pilot plant and stored in a 5000 gallon tank (19 m^3). The sediments were kept in suspension by circulating the water using a submersible pump. Figure 6 is a schematic diagram of the pilot plant and Table 5 outlines the operating parameters. All wetted or ozone exposed surfaces were built of only stainless steel, Teflon, or glass. Flow to the pilot plant was approximately 6.4 L/min. A single, 6-inch (150 mm)diameter glass, counter current ozone contactor was employed. The ozone was generated by an oxygen-supplied PCI model GL-1 generator. Gas-phase ozone was monitored continuously by Ultra-Violet (UV). Liquid-phase ozone residual was measured continuously by an Orbisphere model 26501 monitor which was frequently checked by the indigo trisulfonate method (Bader and Hoigné, 1982). Ozone was applied such that the ozone/TOC ratio was near 0.7 mg/mg. A transfer efficiency greater than 95 percent was maintained. The dissolved ozone residuals in the contactor effluent ranged between 0.2 to 0.4 mg/L and 0.05 to 0.2 mg/L after rapid mixing.

Alum was used as a coagulant to control particulates. Alum doses were determined by jar testing of water collected from the ozone contactor with each truckload of water. The rapid mixer was operated at 100 rpm with a 2 minute detention time. Alum treatment lowered the pH from 8.0 to 7.5, and subsequent processes had little affect on in pH. A four stage flocculator followed which used tapered mixing decreasing from 30 to 18 to 14 to 8 rpm. A rectangular sedimentation tank with a 5.75 hour detention time was used. Sludge was removed by vacuuming biweekly and settled turbidities ranged from 1 to 3 ntu.

Following sedimentation, the flow was split to 8 parallel glass filters. The filters were designed to supported a dual media of anthracite and sand, GAC and sand or a single medium (in this case only sand). All filters were supported by 8 inches (200 mm)of gravel and 4 inches (100 mm) of coarse sand. Design loading rates and EBCTs for all filters were 2 gpm/ft^2 (5 m/h) and 9.2 minute (30-inch (760 mm) media depth) respectively. Filters 1, 2 and 3 were 6-inch (150 mm) diameter; Filters 4 through 8 were 1.5-inch (38 mm) diameter. Filters 1 and 2 allowed a study of the effects of chlorination on biological activity. Chlorine was applied prior to Filter 1, and Filter 2 was backwashed with chlorinated water. Free chlorine residuals in the backwash water were near 1.0 mg/L. Filters 3 and 4 allowed a comparison of filter performance in larger and smaller diameter filters. Filters 4 through 8 allowed a comparison of biological activity where different media were employed. Filter turbidities were typically in the range of 0.1 to 0.3 ntu. Filters were backwashed when headloss exceeded 60 inches (152 mm), or approximately 24 hours before weekly sampling but never longer than every fourth day. Filters were backwashed for 10 minutes with 50 percent bed expansion. No air or water scour was provided during backwash

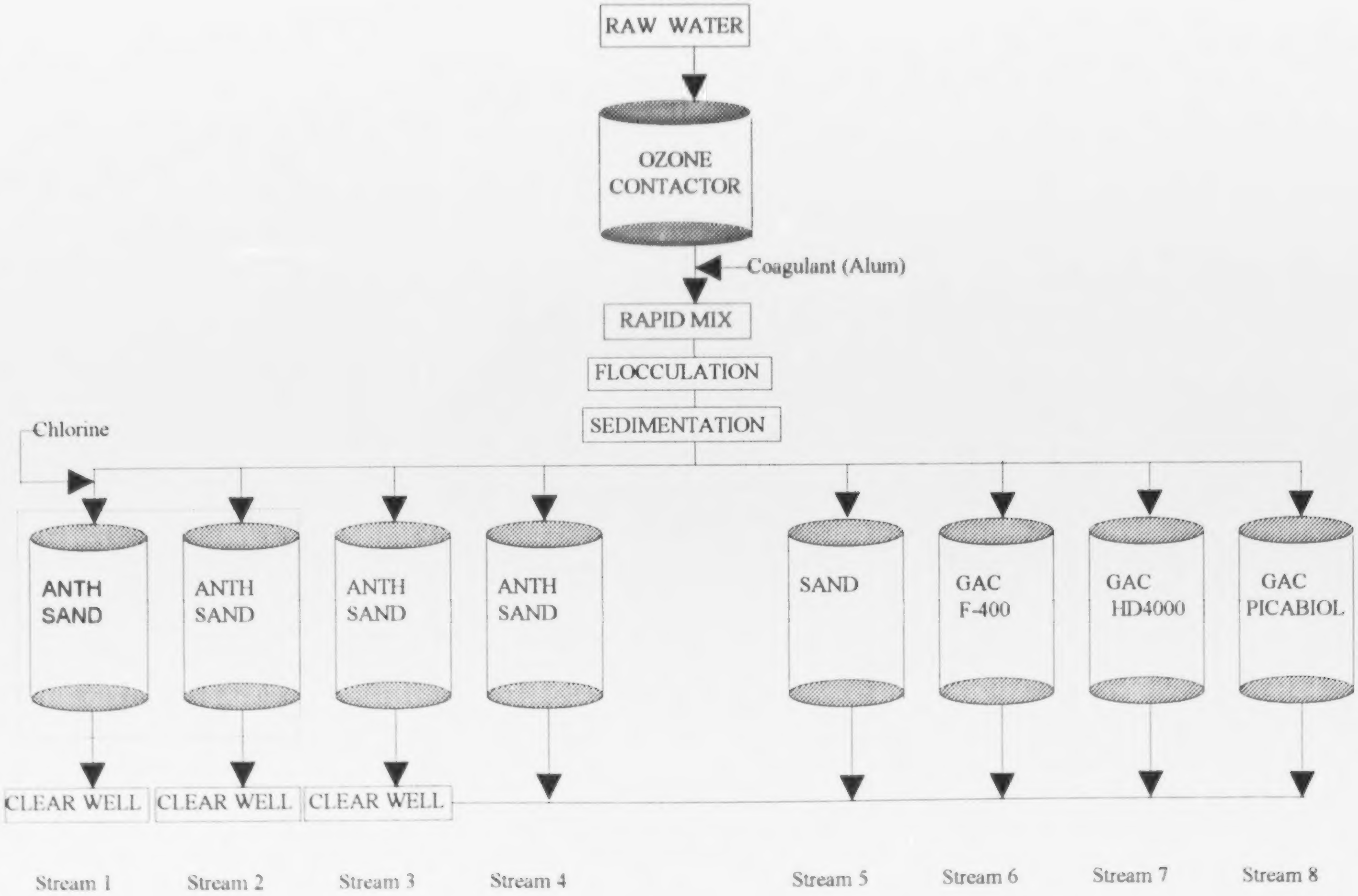


Figure 6: Schematic for the Cincinnati, Ohio Pilot Plant

Table 5
Operating Parameters for Cincinnati, Ohio Pilot Plant (Miltner and Summers 1992)

Treatment Step	Parameter	Value
Raw water	Flow rate	6.4 L/min
Ozonation	Detention time	7.4 min
	T_{10}	2.27 min
	Water depth	8.67 ft (2.64 m)
	Applied Dose	ozone/TOC:0.7 mg/mg
	Transfer Efficiency	> 95 %
Coagulation	Detention time	2 min
	Rapid mix speed	100 rpm
	Alum dose	N/A
Flocculation	Detention time	45 min
	Mixing Speeds	30,18,14,8 rpm
Sedimentation	Detention time	5.75 hour
Filtration	Hydraulic Loading (All filters)	2 gpm/ft^2 (5 m/h)
	Anthracite Depth	
	Filter 1,2,3 & 4	20 inches (500 mm)
	Effective Size	1.02 mm
	Sand Depth	
	Filter 1,2,3, & 4	10 inches (250 mm)
	Filter 5	30 inches (760 mm)
	Filter 6,7, & 8	4 inches (100mm)
	Effective Size	0.44 mm
	GAC depth	
	Filter 6,7 & 8	26 inches (660 mm)
	Effective Size	
	Filtrasorb 400	0.64 mm
	Hydrodarco 4000	0.68 mm
	Picabiol	1.52 mm

N/A - not available

4.6 Edmonton, Alberta 1992-1993

The main focus of this thesis was with the ongoing biological treatment pilot plant in Edmonton, Alberta, operating in 1992 to 1993. There were two phases scheduled for this study, however only the first phase was considered in this thesis and will be the only phase described below. Much of the front end of the treatment process was similar to the 1989-1990 study, however several significant changes had been made after filtration. Figure 7 is a schematic of the pilot plant and Table 6 outlines the operating parameters. All materials in contact with water were made of stainless steel, glass or a fluorocarbon to prevent organic contamination. Appendix A provides further details of the pilot plant.

Raw water for the pilot plant was obtained from the North Saskatchewan River at the intake to the Rossdale Water Treatment Plant. Raw water flowed to the pilot plant at 40 L/min passing through a screen to remove stones and leaves. A presedimentation tank provided protection from periodic high raw water suspended solids levels and a blowdown flow of 10 percent of influent flow was maintained. Coagulation was achieved with polyaluminum chloride with a dosage ranging from 20 to 120 mg/L, but normally in the range of 20 to 30 mg/L. Rapid mixing was accomplished with a variable speed agitator with a detention time of 17 seconds. A three stage tapered flocculation followed with a detention time of 37 minutes. A tapered velocity gradient was achieved with impeller speeds of 40, 20, and 12 rpm. Clarification was completed in a sedimentation tank containing of 60 ° parallel plates, spaced at 50 mm intervals.

Following sedimentation a settled water storage tank served to split the flow, buffer variations in flow and provide a constant head for pumping to downstream processes. Part of the settled water was then pumped into an ozone contactor operating in a counter current mode. This contactor was designated contactor 2; contactor 1 would be utilized in Phase 2. The dose applied to contactor 2 was initially 1.0 mg/L ozone per mg/L NVOC, however, in March 1993 the approach was shifted to maintain a target ozone residual, which lowered the applied dose to approximately 0.75 mg/L ozone per mg/L NVOC. Ozonated water from contactor 2 was directed to a small dissipation tank to allow a longer contact gas/water contact time and permit decay of the residual ozone prior to filtration. At this point the ozonated water was pumped to two anthracite-sand filters (Filters 2 and 3) and one GAC F-300-sand filter (Filter 4). Two other streams originated from the settled water storage tank. One stream, considered the control stream, was pumped to filter (Filter 5) with no ozonation. The final filter (Filter 1) was chlorinated to obtain a residual of 0.5 mg/L free chlorine prior to filtration.

For all filters, filtration was carried out in the constant-rate, variable-head mode. Filters 3 and 4 received a hydraulic loading of 5 m/h and Filters 1,2 and 5 received a hydraulic loading of 10 m/h. Filters 1, 2, 3 and 5 contained 610 mm anthracite overlying 305 mm sand, and the filter adsorber (Filter 4) contained 610 mm GAC F-300 overlying 305 mm sand. The columns were backwashed manually every 24 hours and also employed an air scour system during backwash.

Filtered water was then pumped to the GAC contactors, also operating at a constant rate, variable head mode. Contactors 2, 3 and 4 contained approximately 2.3 m of F-400[5] and contactor 4 contained approximately 2.3 m of Pica[6]. Contactors 3 and 4 received a hydraulic loading of 4 m/h and contactors 2 and 5 received a hydraulic loading of 8 m/h. The columns had five sampling ports which represented contact times varying from 1 to 17.5 min at the high loading rate and 1 to 34.5 min at the low loading rate. The dual-media filters and GAC contactors were backwashed with effluent from each respective stream.

As with the previous Edmonton study, the spring run-off event was intensely sampled to obtain higher concentrations for all parameters measured for. The spring runoff event occurred in late March, where raw water colours peaked at 44 TCU. Turbidity levels peaked in late April and exceed values of 200 NTU. The biological treatment process was able to successfully operate during the spring runoff period. Therefore target effluent turbidities were able to maintained during the period of higher influent turbidity.

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[5] Filtrasorb 400, Calgon Corp., Pittsburgh, Pa

[6] Nuchar Activated Carbon(PICA), Westvaco, Covington, Virginia

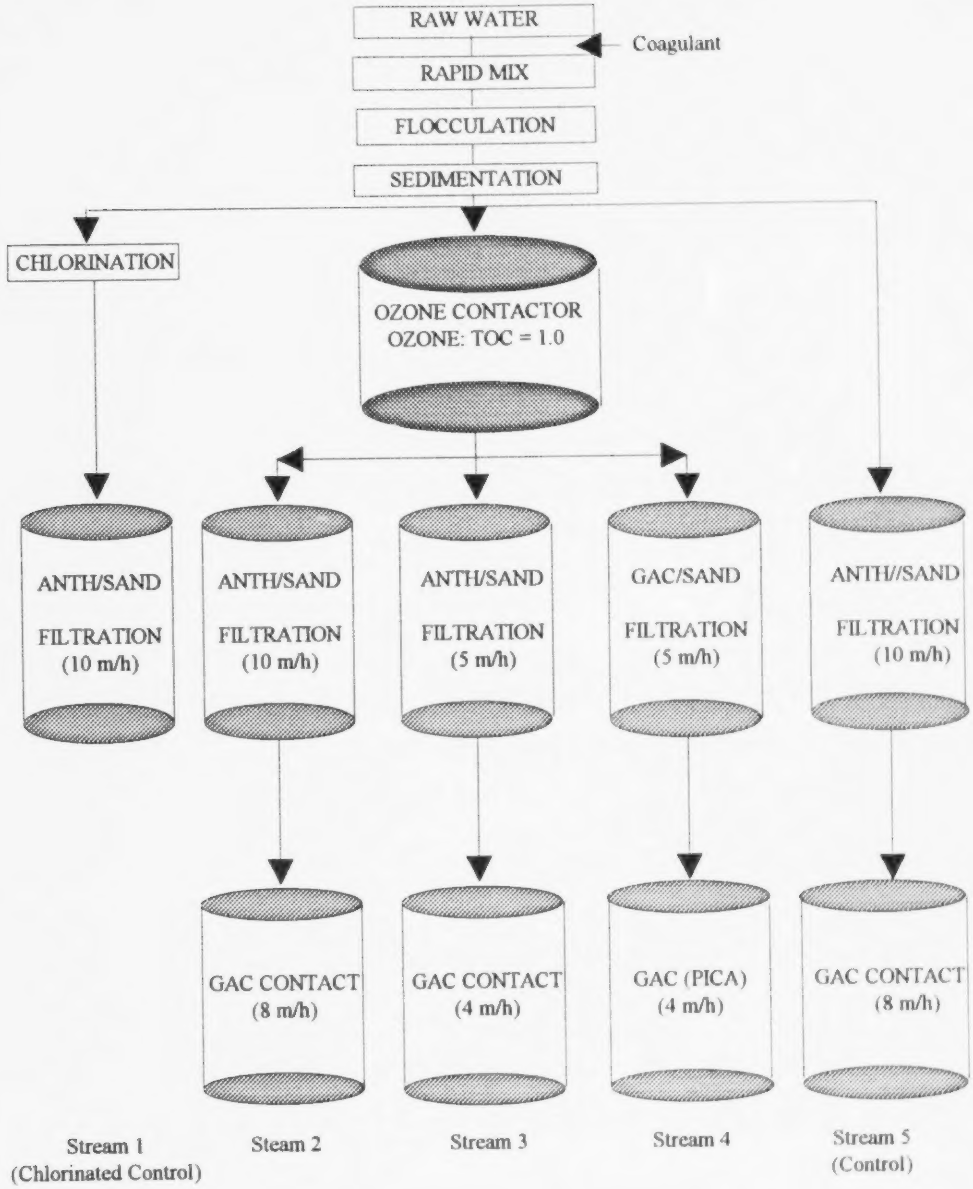


Figure 7: Schematic for the Edmonton, Alberta Pilot Plant 1992-1993 (Phase I)

Table 6;
Operating parameters for Edmonton, Alberta pilot plant (1992-1993)

Treatment Step	Parameter	Value
Raw water	Flow rate	40 L/min
Screening	Screen opening	3 mm
Presedimentation	Overflow rate	4.15 cm/min
	Detention time	9.3 min
Coagulation	Detention time	17 s
	Polyaluminum Chlorine Dosage	20-120 mg/L
Flocculation	Detention time	37 min (3 units total)
	Velocity gradient	40, 20, 12 rpm
Sedimentation	Parallel plates	60 ° inclination
	Plate separation	5 cm
	Detention time	69.8 min
Settled-water storage	Detention time	15.5 min
Ozonation	Detention Time- Contactor 2	16.3 min
	Applied dose (target)	
	Contactor 2 to filters 2,3 & 4	0.75 -1.0 mg ozone/mg NVOC
Filtration	Anthracite depth (Filter 1,2,3 &5)	610 mm
	Effective size	1.18 mm
	Sand depth (Filters (1,2,3,4, &5)	305 mm
	Effective size	0.45 mm
	GAC f-300 depth (Filter 4)	610 mm
	Effective size	0.75-0.85 mm
	Hydraulic loading	
	Filter Columns 3 and 4	5 m/h
	Filter Columns 1,2 and 5	10 m/h
GAC columns	Carbon	
	Type (Column 2,3,&5)	GAC
	Effective size	0.55-0.75 mm
	Sieve size	12-14 (US standard)
	Pore volume	0.94 cc/g
	Uniformity coefficient	1.9 (maximum)
	Particle density wetted-water	1.3-1.4 g/cc
	Total surface area (N_2 BET)	1050-1200 mm^2/g
	Bed depth	
	Contactors 2,3,4 and 5	2.8 m
	EBCT-Column 3 and 4	1-34.5 min
	EBCT-Column 2 and 5	1-17.3 min
	Hydraulic Loading	
	Column 3 and 4	4 m/h
	Column 2 and 5	8 m/h

4.7 Comparison Among Pilot Plants

Table 7a summaries the parameters analyzed for the pilot studies investigated. This table illustrates that the Edmonton, 1992-1993 study provided the most information. The Edmonton, 1989-1990 and Laval studies provide some BOM and chlorinated by-product precusor parameters, Cincinnati provided one parameter from each class of compound, the Southern California provided aldehyde compounds, and the Woodbridge study generally provided several parameters for each class of compound.

Table 7a
Summary of Parameters Analyzed for the Pilot Studies Investigated

Parmeter	Edmonton 1989-90	Laval, Quebec	Cincinnati, Ohio	Southern, California	Woodbridge, Connecticut	Edmonton, 1992-93
TOC	X	X			X	X
AOC	X	X	X		X	X
BDOC		X				X
DCAAFP			X			X
TCAAFP					X	X
CHFP						X
AOXFP	X					X
THMFP	X	X				X
Chlorine Demand	X	X				X
Formaldehyde				X	X	X
Methyl Glyoxal			X	X	X	X
Glyoxal				X	X	X
Acetadehyde					X	X
Propanal						X
Ketomalonic Acid						X
Oxalacetic Acid						X
Pyruvic Acid					X	X
Glyoxylic Acid					X	X

Table 7b summarizes the operational parameters for all investigated studies. These studies obtained raw water for their biological water treatment studies from different sources except the Edmonton studies, which used the same raw water source but during different years. The raw water temperature varied between studies with the warmest temperature being reported for Cincinnati and Southern California, and the coolest temperatures reported during the Laval study.

The Edmonton and Laval studies reported the most extreme raw water TOC concentration range. The TOC and DOC concentrations for the remaining studies averaged around 2.5 mg/L. Different coagulants were employed in the various studies. The Edmonton studies employed Aluminex, Southern California employed alum plus polymer, and the remaining studies employed only alum. The coagulant dose varied, with the highest dose being applied in the Edmonton studies.

The raw water AOC concentration was found to be the highest for the Laval study. However, the Laval study had reported their raw water AOC with AOC-NOX expressed in equivalent carbon units as oxalate. All other studies indicated a similar range of raw water AOC concentrations. In general, the AOC-P17 was the highest component of the total AOC in most studies, except Southern California.

The ozone dosage varied with the highest dose being applied in the Edmonton studies. The ozone dosage for most of the studies was monitored by ozone residual, and from all information obtained it would appear that similar ozone dosages and residuals were employed in the various studies. The contact time depended on ozone contactor size and feed rate and ranged between 7.4 and 16.3 minutes.

The AOC concentration after ozonation generally increased in all cases, except for the Edmonton studies. Although the Edmonton studies reported lower AOC concentrations, they also ozonated prior to filtration. The other studies reporting higher AOC concentrations ozonated prior to coagulation (except Laval). Therefore, it is assumed some AOC removal has occurred during the coagulation, flocculation and sedimentation steps in the case of the Edmonton studies. In general, the AOC- NOX component of total AOC was the highest in all studies after ozonation.

All studies employed a first stage filtration step, and in the current Edmonton (1992-1993), Southern California, Woodbridge and Cincinnati studies, GAC/sand filters in addition to anthracite/sand filers were utilized. The first stage filtration bed depth was similar in most cases and averaged 780 mm. A second stage filtration step was employed only in the Edmonton and Laval, Quebec studies.

The backwashing procedures varied among studies. Typically, filter backwashing was completed daily. Only the Edmonton 1992-1993 study employed an air scour process, and Southern California employed a surface wash. In most cases dual media filter backwashing was completed with non-chlorinated water, with one or two streams backwashed with chlorinated water. Few details were available for GAC contactor backwashing. For the two Edmonton studies backwashing was completed weekly using non-chlorinated water.

Table 7b

Summary of Key Quality Operationsl Parameters for Pilot Plant Studies Investigated

Parameter	**Edmonton 1989-90**	**Woodbridge CT**	**Southern California**	**Laval Quebec**	**Cincinnati Ohio**	**Edmonton 1992-93**
Coagulant	Aluminex	Alum	Alum + Polmer	Alum	Alum	Aluminex
Coagulant Dose mg/L	20-140	N/A	5-6 Alum 3 polymer	30-45	N/A	20-120
Ozonation Step	post clarification	pre-coagulation	pre-coagulation	pre- BAC filtration	pre-coagulation	post clarification
Ozone Dose	0.5 or 1.0 mg/ mg NVOC	0.5-1.0 mg/L	1.0-1.8 mg/L	1.5 mg/L	0.7 mg/mg TOC	0.75-1.0 mg/mg NVOC
Ozone Contact Time	10	N/A	N/A	8	7.4	16.3
Filtration Media	Anth/Sand	Anth/Sand GAC/Sand	Anth/Sand GAC/Sand	Anth/Sand	Anth/Sand GAC/Sand	Anth/Sand GAC/Sand
Media Depth (mm)	750	760	711	800	760	910
Hydraulic Loading Rate (m/h)	5-10	3.75-7.5	7.5-22.5	4-10	5	5-10
EBCT (min)	4.5-9	6.1-12.2	1.9-5.7	4.8-12	9.1	5.5-11
Filter Backwashing						
Frequency	daily	N/A	daily (rate dependent)	N/A	daily	daily
Type of Water	non-chlorinated	chlor + nonchlor	chlorinated (0.2 mg/L)	N/A	chlor + nonchlor	chlor + nonchlor
Air Scour	no	N/A	no	N/A	no	yes
Surface Wash	no	N/A	yes	N/A	no	no
Bed Expansion	N/A	N/A	20-30 %	N/A	50%	20-30%
GAC Media	F-400	none	none	F-400	none	F-400/Pica
Media Depth (m)	2.7-2.8	none	none	2	none	2.3
Hydraulic Loading Rate (m/h)	4.8	none	none	4-10	none	4-8
EBCT (min)	2-40	none	none	2-30	none	1-35
GAC Backwashing						
Frequency	weekly	not applicable	not applicable	N/A	not applicable	weekly
Type of Water	non-chlorinated			N/A		non-chlorinated
Air Scour	no			N/A		no
Surface Wash	no			N/A		no
Bed Expansion	N/A			N/A		0.2
Raw Water TOC (mg/L)	1.6-11	3 (DOC)	2.3-3.7	1.0-20	N/A	1.5-7.5
Raw Water Temperature (C)	N/A	N/A	11-25	1-20	12-27	3-15
Raw Water Source	N. Saskatchewan River	West River	CRW/SPW	Milles-Iles River	Ohio River	N. Saskatchewan River
Raw Water Total AOC	20-60	35-53	51-98*	~100 - 700*	N/A	30-80
Raw Water AOC-P17	15-55	17-48	28-85	N/A	N/A	37-75
Raw Water AOC-NOX	5-36	5-18	30-100*	N/A	N/A	7-16
Post Ozonation Total AOC	11-57	57-134	275-613*	200-700*	N/A	20-35
Post Ozonation AOC-P17	2-25	1.3-105	30-100	N/A	N/A	1-10
Post Ozonation AOC-NOX	23-52	29-66	125-350*	N/A	N/A	14-20

N/A- information not available

AOC units expressed in ug/L equivalent carbon as acetate

* AOC-NOX units expressed in ug/L equivalent carbon as oxalate

CHAPTER 5
DATA ANALYSIS: RESULTS AND DISCUSSION

The empirical analysis involved plotting the removal rates for each parameters versus the influent concentration of that parameter to the bioreactor. Data for each filter or GAC contactor were plotted separately, since removal rate was found to be proportional to influent concentration. The removal rate was calculated for each parameter using the difference between influent and effluent concentrations and dividing the difference by the EBCT (equation 1). This value was subsequently plotted against influent concentration.

$$\text{Removal Rate} = \frac{\text{(Influent Concentration - Effluent Concentration), } (\mu\text{g or mg})/\text{L}}{\text{EBCT (min)}} \quad (1)$$

These relationships could be represented by a first order process and apparent first-order rate constants were calculated using linear regression. The linear regression was performed using two software packages (Microsoft Excel and Quattro Pro), to provide confidence in the results obtained. The results between the two software packages were found to agree. In addition, the 95% confidence intervals were determined for the apparent first order rate constants and were reported for every parameter in each study. The y-intercepts and their 95% confidence intervals were determined, indicating when the y-intercepts were significantly different than zero. The x-intercept was calculated using the linear regression equation. The x-intercept was assumed to be similar to S_{min} in the biofilm model, which represents the minimal achievable concentration. A lack of fit test was performed for the model for each set of data; however, it was found that often the null hypothesis would be accepted when the correlation coefficient was not significant at the 5% level. It was therefore decided that a test of significance for the correlation coefficient would provide a more rigorous indication of the applicability of the first-order relationship for a given data set.

Occasionally, the data for the 1992-1993 Edmonton study contained some unexplained anomalies. These anomalies were events where an effluent concentration was a factor of 10 above its expected value and were only noted for AOC and some of the aldehydes. It was decided to delete these points for this analysis since they only occurred during one sampling event which corresponded to the spring runoff event. Typically when a concentration increased after filtration, the negative removal was accepted and used in the analysis. Only when an unusually high increase occurred was it removed from the data set.

When the linear relationship between removal rate and influent concentration was poor and correlation coefficients were not significant at the 5% level, the residuals were plotted against influent concentration to examine whether another relationship could better fit the data. No such relationship suggested itself in this study. All removal rate versus influent concentration plots for all parameters in each study are found in Appendix B. The plots show the linear relationship, the regression line equation and correlation coefficient. The following section presents and discusses the results of this analysis for every parameter in each study, except for oxoacids which were present in very low concentrations. Because useful relationships were not obtained for these parameters, and to reduce the size of the body of the thesis, the oxoacid analysis in included as Appendix C. Chapter 5 only displays selected figures from Appendix B for parameters from each study. Comparisons among parameters will be made in Chapter 6.

5.1 Total Organic Carbon (TOC)

The measurement of TOC is commonly reported in biological drinking water treatment studies. Of the studies investigated, the specific parameters reported were nonvolatile organic carbon (NVOC) for the Edmonton studies, TOC for the Laval study and dissolved organic carbon (DOC) for the Woodbridge, CT study.

Edmonton, Alberta 1989-1990

The Edmonton, Alberta, 1989-90 study reported NVOC for the influent and effluent of four dual media filters and four GAC contactors. These data had been previously analyzed, using seasonal averaged values (Huck and Anderson, 1992). These data were re-analyzed using individual data points, and apparent first-order rate constants and y-intercepts were calculated with their 95% confidence intervals (Table 8). The correlation coefficients were also calculated and the significance levels determined. The x-intercepts were calculated to estimate the minimum achievable concentration. The results of this analysis are displayed graphically in Appendix B, Figures B1 and B2.

Because of the extremely large number of rate constants calculated in this thesis, formal comparisons using the 95% confidence interval were not carried out. The confidence interval does however indicate how closely each rate constant is estimated.

A large number of tables similar to Table 8 will be presented in this chapter. For uniformity, a consistent set of footnotes regarding levels of the correlation coefficients is used for all such tables, even though all footnotes may not apply to all tables.

Table 8

NVOC Summary for Edmonton, 1989-90 Study

Stream	Apparent Rate Constant* (min^{-1})	x-intercept (mg/L)	y-intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.020 ± 0.007	0.10	-0.002 ± 0.023	0.63	9
Filter 2	0.039 ± 0.012	0.82	-0.032 ± 0.039	0.73	4.5
Filter 3	0.025 ± 0.006	0.40	-0.010 ± 0.021	0.75	9
Filter 4	0.020 ± 0.013	0.05	-0.001 ± 0.045	0.44	4.5
GAC 1	0.026 ± 0.001	0.07	-0.002 ± 0.004	0.99	36
GAC 2	0.048 ± 0.010	0.92	-0.044 ± 0.029	0.81	19
GAC 3	0.026 ± 0.003	0.50	-0.013 ± 0.009	0.91	36
GAC 4	0.046 ± 0.009	0.72	-0.033 ± 0.028	0.83	19

* Apparent first order rate constants and y intercepts are shown with 95% confidence intervals.

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, the dual media filters were fed at two hydraulic loading rates, 5 and 10 m/h. In addition, two ozone dosages were employed: the ratio of ozone dose to NVOC was either 0.5 or 1.0 mg/mg. Figure 8 displays a typical relationship for a first stage filtration for Filter 3. The calculated apparent first-order rate constants varied from 0.020 to 0.039 min^{-1} for all four filters. The correlation coefficients varied between 0.44 to 0.75 and all correlation coefficients were significant at at least the 1% level. The x-intercept varied between 0.05 to 0.82 mg/L, indicating the minimum achievable concentration. However, for NVOC, which contains a non-biodegradable component, the x-intercept may not be physically meaningful. Although the correlation coefficient was quite low in the case of Filter 4, it was still significant at the 1% level since the degree of freedom for all of these filters was around 50. Huck et al (1991) discuss reasons for poor performance of this filter. The first order rate constants appear to vary according to the EBCT, with the exception to Filter 4 (due to its poor linearity). In general, the higher the EBCT, the lower the apparent first-order rate constant. This observation would indicate that approximately the same degree of NVOC removal was achieved for both hydraulic loading rates, and at the low hydraulic loading rate. Little removal was achieved in the lower portion of the bed.

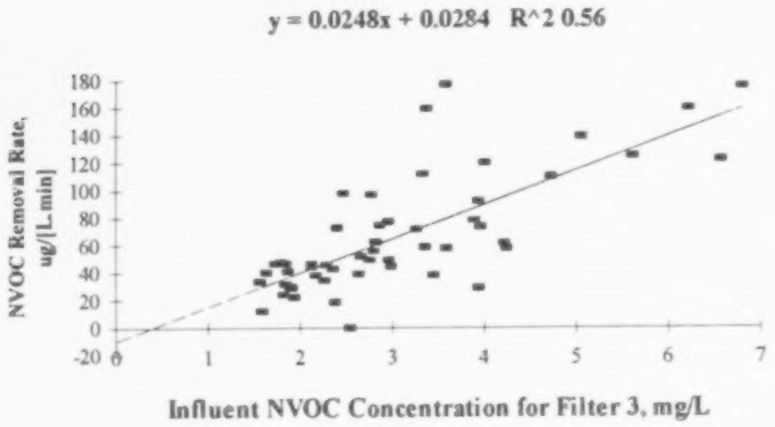


Figure 8: NVOC Removal Rate vs. Influent Concentration for Filter 3, Edmonton, 1989-90 Study

For the second stage filtration, the effluent from the dual media filters was fed to the GAC contactors at two hydraulic loading rates, 4 and 8 m/h. The results gave apparent first order rate constants varying from 0.026 to 0.048 min $^{-1}$. The correlation coefficients indicated good linearity, varying from 0.81 to 0.99. All the correlation coefficients were significant at least to the 1% level. The x-intercept varied between, 0.05 and 0.92 mg/L, although as discussed previously its meaning maybe questionable for NVOC. As with the dual media filtration, the apparent first-order rate constants appear to be dependent on flowrate, therefore showing little advantage to the longer EBCTs. For the GAC contactors it was noted that there appeared to be two distinct subsets of data and therefore two different apparent rate constants. This can be seen in Figure 9. The data were separated into two seasons, being May to October and November to April. Analysis of this data revealed higher correlation coefficients. The results indicated higher apparent rate constants for the season from May to October (0.028 to 0.055 min $^{-1}$) than for the November to April season (0.021 to 0.31 min $^{-1}$). The could be both due to temperature and to the nature of the NOM present.

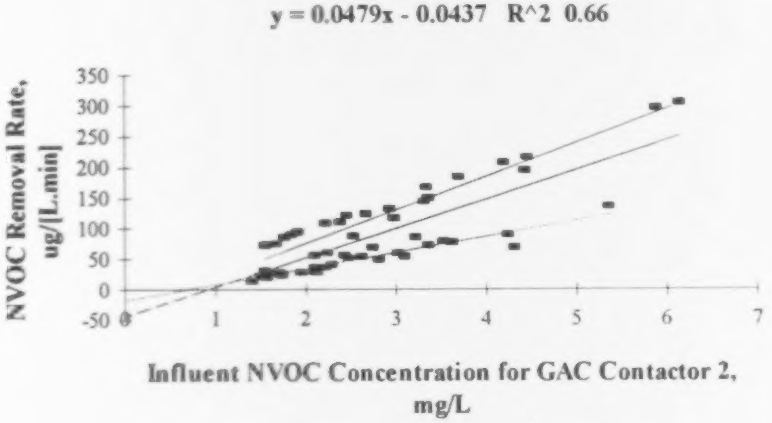


Figure 9: NVOC Removal Rate vs. Influent Concentration for GAC 2, Edmonton, 1989-90 Study

In general, there appeared to be more scatter in the data for the dual media filtration, and better linearity in the GAC contactors. The apparent rate constants appear to be dependent on hydraulic loading rate, and also on seasonal effects. The y-intercepts for all filters and GAC contactors were negative, indicating that there was a minimum concentration below which the NOM could not be reduced biologically. In addition the standard deviation appears to be proportional to the rate constant and to the y-intercept.

Edmonton, Alberta, 1992-1993

The Edmonton, Alberta, 1992-1993 study also reported NVOC for influent and effluent of dual media filters and GAC contactors. The apparent first order rate constant and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercepts were calculated to determine the minimal achievable level. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 9 and a graphical presentation for each filter and GAC contactor is displayed in Appendix B, Figure B3 and B4. It should be noted that the analysis for this study was completed with daily EBCTs calculated from operation data and not design EBCTs used in other studies.

Table 9
NVOC Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (mg/L)	y-intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.014 ± 0.007	0.29	-0.004 ± 0.014	0.85	5.3-5.5
Filter 2	0.023 ± 0.012	0.04	-0.009 ± 0.023	0.85	5.5-6.1
Filter 3	0.027 ± 0.077	0.67	-0.018 ± 0.107	0.44‡	10.8-11.3
Filter 4	0.026 ± 0.011	0.048	-0.001 ± 0.020	0.87	8.8-15.7
Filter 5	0.027 ± 0.034	0.67	-0.018 ± 0.051	0.59‡	5.9-5.5
GAC 2	0.041 ± 0.006	0.15	-0.006 ± 0.010	0.98	17.2-18.4
GAC 3	0.025 ± 0.013	0.36	-0.009 ± 0.015	0.89	34.5-38.1
GAC 4	0.017 ± 0.003	0.35	-0.006 ± 0.004	0.97	34.5-42.7
GAC 5	0.056 ± 0.021	0.64	-0.036 ± 0.033	0.91	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals.

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, stream 1 represented a chlorinated stream, with a free chlorine residual of 0.5 mg/L prior to filtration. Streams 2, 3 and 4 were ozonated streams with an ozone dosage of 1.0 mg ozone/ mg NVOC reduced to 0.75 partly through study. Stream 5 was a non-ozonated stream. The hydraulic loading rates varied, with Filters 1,2 and 5 being fed at 10 m/h and Filters 3 and 4 being fed at 5 m/h. For Filter 5, the non-ozonated stream, the apparent rate constant was 0.027 min^{-1}. A correlation coefficient of 0.59 was determined and was not significant at the 5% level. The chlorinated stream was determined to have an apparent first order rate constant of 0.014 min^{-1} and a correlation coefficient of 0.85 which was significant at the 1% level. The calculated apparent rate constants for the ozonated streams ranged from 0.023 to 0.027 min^{-1} and correlation coefficients ranged from 0.44 to 0.87, where the coefficient for Filter 4 was not significant at the 5% level. The x-intercept ranged between 0.038 to 0.67 mg/L, approximately the same as in the previous study. The results for these filters showed a fair amount of scatter in the data, as seen in Figure 10, however for ozonated streams, the apparent rate constant appeared to be independent of the hydraulic loading rate. The lowest apparent rate constant occurred in the chlorinated stream, as would be expected.

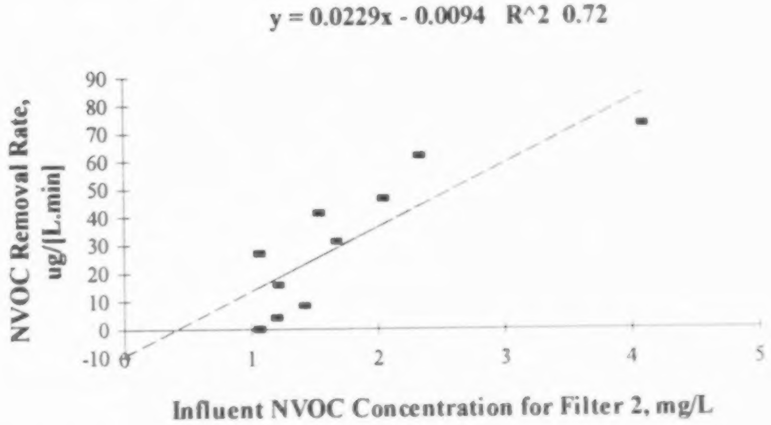


Figure 10: NVOC Removal Rate vs. Influent Concentration for Filter 2, Edmonton, 1992-93 Study

For the second stage filtration, the GAC contactors were hydraulically loaded at two rates, 4 and 8 m/h. The results gave apparent first order rate constants varying from 0.017 to 0.056 min^{-1}. The x-intercept ranged between 0.15 to 0.64 mg/L being approximately the same as for the first stage filtration. All the GAC contactors showed good linearity, and all correlation coefficients were significant at least at the 1% level. The linear relationship for GAC 5 is displayed in Figure 11. The Pica carbon (GAC 4) had the lowest apparent rate constant and the non-ozonated stream (GAC 5) had the highest apparent rate constant. The result for stream 4 could be due to higher removal at the first stage filtration and subsequently a lower apparent rate constant resulting at the second stage filtration. The non-ozonated stream (Stream 5) would remove less at the first stage filtration, resulting in a higher apparent rate constant for the second stage.

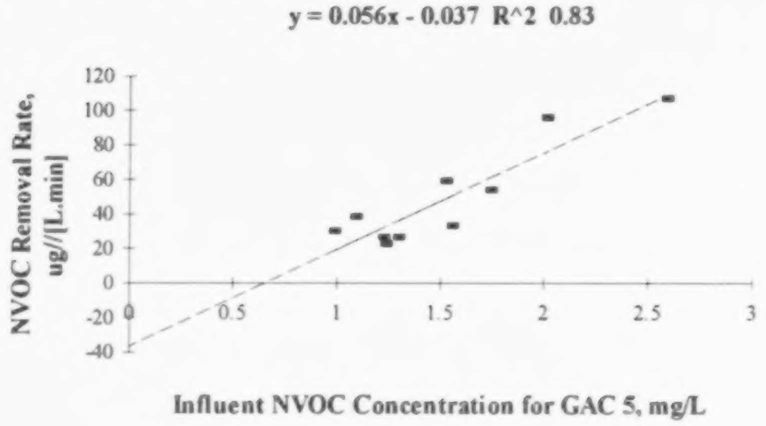


Figure 11: NVOC Removal Rate vs. Influent Concentration for GAC 5, Edmonton, 1992-93 Study

In general it would appear that during the first stage filtration, the apparent first order rate constant appears to be independent of hydraulic loading, whereas during second stage filtration it appears to be dependent on hydraulic loading. Therefore, the higher EBCTs would typically show lower apparent rate constants. This dependence on EBCT corresponds with the results for both filters and GAC contactors in the 1989-90 study (Table 8), indicating that little removal was achieved in the lower portion of the bed at the lower hydraulic loading.

Table 10 displays the results from a profile of NVOC concentrations at various positions of streams 2 and 4 during a spring run-off event. The calculated rate constants are therefore based on only a single set of samples. Both the cumulative apparent rate constants within each stage and the segment apparent rate constants were calculated. For stream 2, the results indicated higher rate constants in the top of the bed in the filter, decreasing with depth. The apparent rate constants at various depths in the GAC 2 contactor also showed the same relationship. For stream 4, the apparent rate constants show the same relationship as seen in stream 2. In general, stream 2 (low EBCT) showed higher apparent rate constants than stream 4 (higher EBCT), which was consistent with what was observed in the above analysis for the GAC contactors. It should be also noted that these results do not indicate a depth at which the apparent segment rate constant became constant in the GAC contactors.

Table 10

NVOC Profile Results for Streams 2 and 4

Location	NVOC (mg/L)	Cumulative Apparent Rate Constants (min^{-1})	Segment Apparent rate Constants (min^{-1})
Following Ozonation	2.332		
Filter 2-31cm	2.024	0.067	0.067
Filter 2-61cm	2.187	0.016	-0.042
Filter 2-91 cm	1.979	0.026	0.051
GAC 2-10 cm	1.570	0.276	0.276
GAC 2-47cm	1.150	0.119	0.096
GAC 2-230cm	0.047	0.044	0.042
Following Ozonation	1.742		
Filter 4-31cm	1.325	0.062	0.062
Filter 4-62cm	1.161	0.044	0.032
Filter 4-91cm	0.850	0.029	-0.001
GAC 4-23cm	0.790	0.076	0.076
GAC 4-47cm	0.503	0.045	0.019
GAC 4-230cm	not available	0.016	0.013

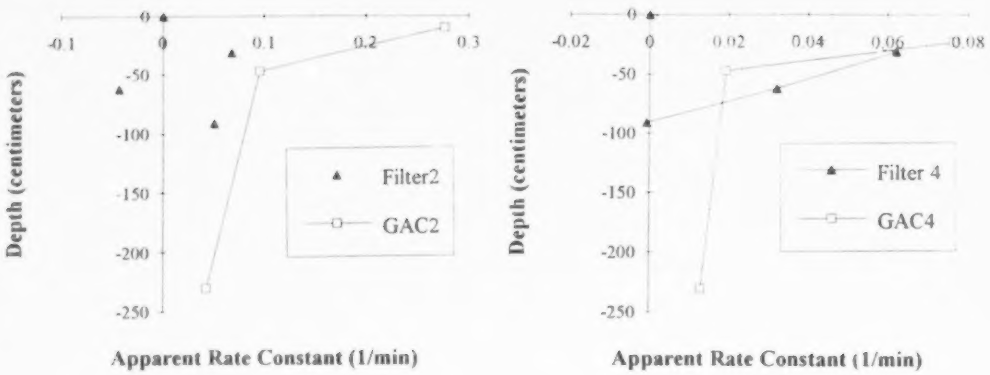


Figure 12: NVOC Apparent Rate Constant Profile for Stream 2 and 4, Edmonton, Alberta, 1992-1993

Laval, Quebec

The Laval, Quebec study measured TOC using a Dohrmann DC 80 analyzer. Although strictly speaking this parameter was not the same as NVOC, it could be considered similar when comparing results from the Edmonton, Alberta studies. The Laval study consisted of a two stage filtration treatment employing dual media filters and GAC (BAC) contactors. The ozonation step was employed prior to BAC filtration. Adequate data were not available for the dual media filtration, however, data for the two BAC contactors was available in addition to profile data. The second stage filtration employed a design hydraulic loading rate of 4 m/h. Individual EBCTs for each sampling day were obtained and used in the calculation. Figures 13 and 14 display the graphical analysis for the two contactors. Table 11 summarizes the apparent rate constants, and y-intercepts with their 95% confidence intervals. The x-intercepts were determined to indicate the minimum achievable concentration, although as discussed previously this may not be meaningful in the case of TOC. The correlation coefficients were calculated and their level of significance determined.

Table 11
TOC Summary for Laval, Quebec Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (mg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
BAC 2G 10 cm	0.110 ± 0.097	2.8	-0.306 ± 0.302	0.84†	5.0-7.0
BAC 2G 70 cm	0.041 ± 0.065	2.6	-0.105 ± 0.076	0.92	13.0-16.0
BAC 2G 130 cm	0.025 ± 0.016	2.5	-0.063 ± 0.112	0.91†	20.0-26.0
BAC 2G Effluent	0.019 ± 0.007	2.2	-0.041 ± 0.021	0.97	28.0-36.0
BAC 5D 15 cm	0.107 ± 0.065	2.7	-0.285 ± 0.199	0.92†	5.0-6.0
BAC 5D 80 cm	0.042 ± 0.032	2.4	-0.101 ± 0.096	0.88†	13.0-16.0
BAC 5D 140 cm	0.026± 0.021	2.4	-0.062± 0.065	0.86†	20.0-26.0
BAC 5D Effluent	0.016 ± 0.018	1.8	-0.029 ± 0.054	0.78‡	28.0-36.0

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals.

Note the apparent first order rate constants reported in the above table are cumulative (i.e. apply for the portion of the contactor from the influent down to the stated depth)

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

The results for the two BAC contactors gave apparent first order rate constants of 0.016 and 0.019 min^{-1}. The correlation coefficient for BAC 2G was significant at the 1% level however the correlation coefficient for BAC 5D was not significant at the 5% level.

The x-intercepts were 1.8 mg/L for BAC 2G and 2.2 mg/L for BAC 5D. Apparent rate constants were determined for three locations along the depth of these contactors. These were cumulative constants (i.e. calculated for the portion of the contactor from the surface down to the stated depth). The data used for these calculations are not shown in Figures 13 and 14. The rate constants averaged 0.108 min^{-1}, for a depth of 12.5 cm, 0.041 min^{-1} for a depth of 75 cm and 0.025 min^{-1} for depth of 135 cm. These profile results had correlation coefficients significant at the 5% level or better. These results indicate a greater removal rate near the top of the contactors with decreasing removal rates with depth in the contactor as would be expected. Since the cumulative apparent rate constants continued to decrease with depth, this could indicated that additional depth in the contactor could potentially remove more TOC, but at a much slower rate.

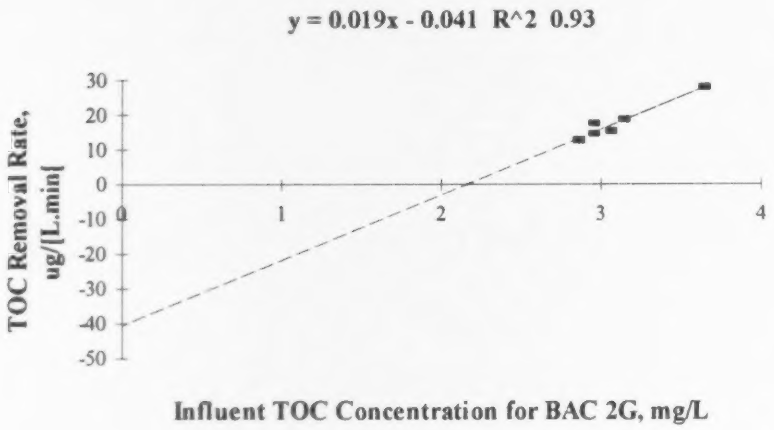


Figure 13: TOC Removal Rate vs. Influent Concentration for BAC 2G, Laval, Quebec Study

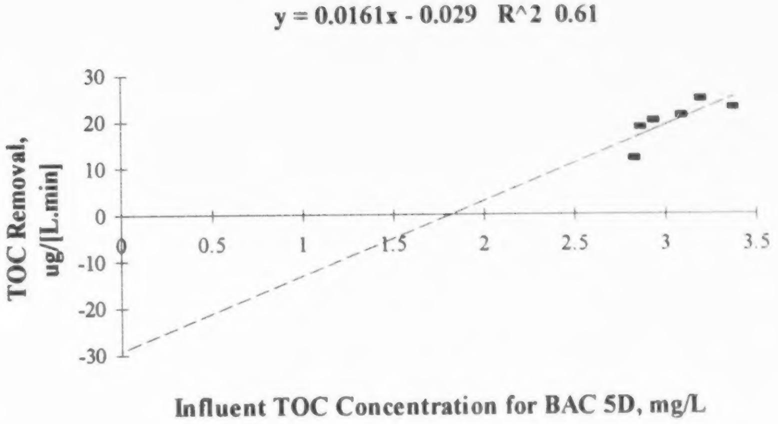


Figure 14: TOC Removal Rate vs. Influent Concentration for BAC 5D, Laval, Quebec Study

The apparent rate constants were also determined for each individual segment along the depth of the column. This profile is shown in Figure 15. These apparent rate constants were determined from approximately six data points; however, it was noted that after the 15 cm depth the correlation coefficients were not significant at the 5% level. This observation indicates that the removal below 15 cm in the contactor was variable between the sampling events. This figure shows that the greatest removal is achieved in the first 10 or 15 cm for both BAC 2G and 5D. For BAC 2G the apparent rate constants appeared to decrease with depth and slightly increase near the base of the contactor. For BAC 5D the apparent rate constant decreased at 80 cm, then appeared to significantly increase at 140 cm, then decrease at the base of the contactor. In general BAC 2G indicated better linearity than BAC 5G. Although not statistically significant, it would be expected that the relationship observed in BAC 2G would better represent the actual profile in the contactor, since the apparent rate constant would be expected to decrease with depth.

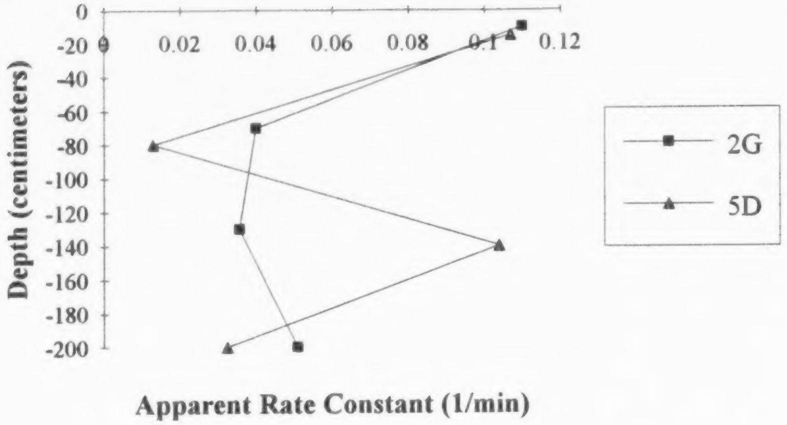


Figure 15: TOC apparent first order rate constant profile for BAC 2G and 5D, Laval, Quebec Study

Woodbridge, CT

The Woodbridge study reported DOC instead of TOC. Samples for analysis of DOC were filtered with a Whatman GF/F glass fiber filter prior to determination. The persulfate-ultraviolet oxidation method (#5319 C, APHA-AWWA-WPCP, 1989) was used for measuring DOC.

It should be noted that design hydraulic loading rates were used in the analysis of these data. Unfortunately, the hydraulic loading rate was doubled for two sampling days during the study, and at the most a total of five sampling points were provided. The apparent rate constants were calculated with their 95% confidence intervals for each stream. The x-intercepts were calculated to estimate the minimal achievable concentration. Again, this value maybe of questionable physical significance for DOC. The correlation coefficients and their level of significance were determined. The results are displayed graphically in Appendix B (Figure B6), and a tabular summary is provided in Table 12. The results for Filter 1 are shown in Figure 16.

Table 12

DOC Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (mg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.240 ± 0.154	1.8	-0.427 ± 0.269	0.98	6.2-12.2
Filter 2	0.277 ± 0.071	1.9	-0.516 ± 0.830	0.92‡	6.2-12.2
Filter 3	0.299 ± 1.608	2.0	-0.593 ± 4.196	0.91‡	6.2-12.2
Filter 4	0.301 ± 0.255	1.9	-0.583 ± 1.219	0.91†	6.2-12.2
Filter 5	0.340 ± 0.244	2.1	-0.704 ± 0.609	0.93†	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

This study only employed a first stage filtration, which consisted of four dual media filters with GAC/sand and a fifth filter containing anthracite/sand. All filters were fed at a hydraulic loading rate of 3.75 m/h, which was increased to 7.5 m/h for two sampling events. Two GAC/sand filters were ozonated prior to filtration and the other three filters received no ozonation. An ozonated stream and a non-ozonated stream were backwashed with chlorinated water. The results of this study gave apparent rate constants ranging from 0.24 to 0.34 min^{-1}. The x-intercepts ranged between 1.8 and 2.1 mg/L, the lowest concentrations being for the ozonated filters. The correlation coefficients ranged from 0.91 to 0.98, and were all significant at least at the 5% level except for Filters 3 and 4. These filters were not ozonated and Filter 3 was backwashed with chlorinated water. It was noted that the apparent rate constants for these filters were all within the same range, and the best linearity was found to be with Filter 1.

The apparent rate constants are approximately one hundred times greater than those for TOC and NVOC in the Laval and Edmonton studies. This suggests that the organic matter encountered in this water is much more biodegradable than that in the Laval and

Edmonton studies. It was noted, however that although the hydraulic loading rate varied significantly throughout the testing, generally good linearity was achieved. It was also noted that the y-intercepts for the non-ozonated and anthracite/sand media gave larger negative values, indicating a higher minimum concentration below which the biodegradable material could not be reduced biologically. In addition it was observed that higher removals were achieved by pre-ozonated and GAC filtration.

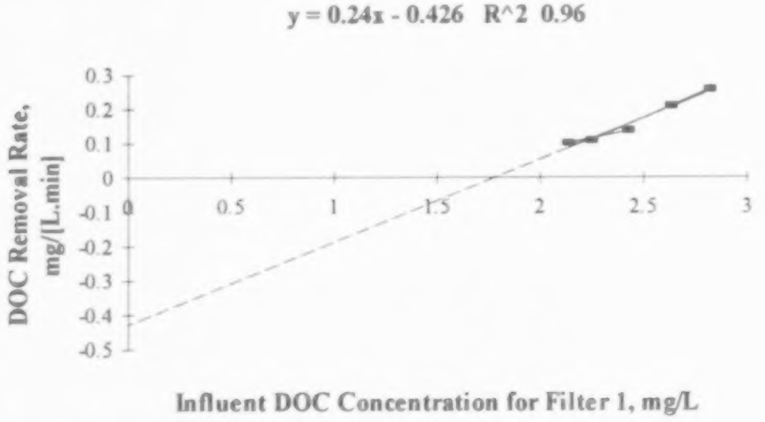


Figure 16: DOC Removal Rate vs. Influent Concentration for Filter 1, Wood bridge, CT Study

Discussion and Comparison for NVOC

In an attempt to discuss and compare the NVOC (TOC) results for all the studies, two graphs were generated. Figure 17 displays the calculated apparent rate constants versus the EBCT and Figure 18 displays the minimum achievable NVOC concentration versus EBCT. These figures were generated using only the apparent rate constants for streams showing significant linearity. These figures do not include the DOC results for the Woodbridge study since the apparent rate constants were determined to be an order of magnitude greater than the NVOC rate constants. It can be said from the Woodbridge study that better linearity and DOC removal was achieved by pre-ozonation and GAC filtration, as was also observed in the other studies. An additional observation from all studies indicated that the first stage filtration appeared to be independent of hydraulic loading rate.

From Figure 17 it can be seen that the rate constant for first stage filtration appear to be independent of EBCT. This figure displays a relatively constant apparent rate constant for the two Edmonton studies, which employed a first stage filtration for EBCT as high as 12 minutes. Observations beyond the 12 minute EBCT include both the Edmonton and the Laval data and would indicate that for second stage filtration apparent rate constants are dependent on EBCT, with the apparent rate constant decreasing with increasing EBCT.

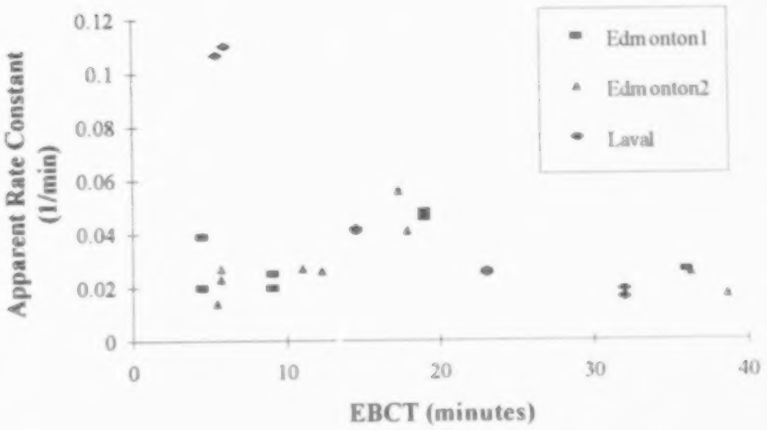


Figure 17: NVOC Apparent Rate Constant vs. EBCT

Figure 18 indicates that there is no apparent relationship between the x-intercept (minimum achievable concentration) and EBCT. This figure does indicate that the x-intercept varied greatly between the Laval and Edmonton studies. The Edmonton studies indicated that approximately the same minimum concentration was achieved independent of EBCT. The Laval study produced higher x-intercepts; however, two notable differences between these studies were found. First the Laval study operated under more extreme water temperatures than the Edmonton study, and generally colder temperatures. In addition, the Laval BAC influent TOC concentration varied between 2.9 and 3.7 mg/L where the combined Edmonton GAC influents varied from < 1.0 mg/L to greater than 5.0 mg/L during spring runoff. These observations would suggest that the minimum achievable NVOC concentration would be sensitive to cold water temperatures.

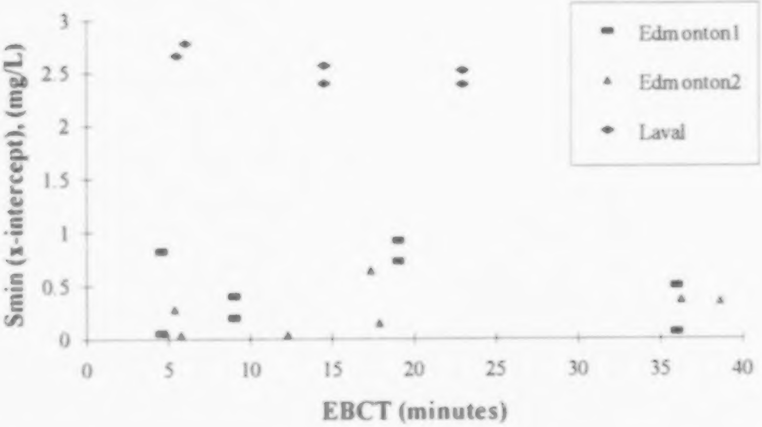


Figure 18: Minimum Achievable NVOC concentration vs. EBCT

5.2 Assimilable Organic Carbon (AOC)

Edmonton, Alberta, 1989-1990

The Edmonton, Alberta, 1989-90 study reported AOC for the influent and effluents for four dual media filters and three GAC contactors. As discussed previously, data for GAC Contactor 1 were unavailable. These data were analyzed using individual data points (Appendix B, Figures B7 and B8) and apparent first-order rate constants were calculated. They are reported with their 95% confidence intervals in Table 13. The x-intercepts were determined to obtain the minimum achievable concentration. The correlation coefficients were also calculated and the significance level determined.

Table 13

AOC Summary for Edmonton, 1989-90 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.075 ± 0.014	5.5	-0.409± 1.709	0.96	9
Filter 2	0.125 ± 0.032	15	-1.882 ± 4.160	0.94	4.5
Filter 3	0.081 ± 0.026	9.0	-0.726 ± 4.376	0.91	9
Filter 4	0.091 ± 0.095	29	-2.644 ± 18.79	0.65‡	4.5
GAC 2	0.037 ± 0.008	2.9	-0.107 ± 0.498	0.94	19
GAC 3	0.022 ± 0.002	5.4	-0.118± 0.155	0.98	36
GAC 4	0.043 ± 0.003	-2.0	0.084 ± 0.704	0.99	19

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals.

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, the dual media filters were fed at two hydraulic loading rates and two ozone dosages were employed. The calculated apparent first-order rate constants varied from 0.075 to 0.125 min^{-1} for all four filters. The x-intercepts values ranged between 5.5 to 29 µg/L. Except for Filter 4 which performed poorly as discussed previously, the correlation coefficients were at least 0.91 and all correlation coefficients were significant at least at the 1% level, except for Filter 4. The first order rate constants appeared to vary according to the EBCT, with the exception of Filter 4. All Filters except Filter 4 showed good linearity and this relationship is shown in Figure 19 for Filter 1.

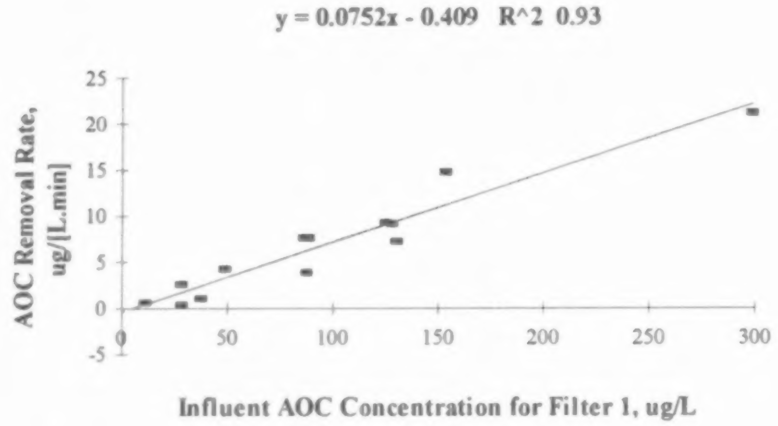


Figure 19 AOC Removal Rate vs. Influent Concentration for Filter 1, Edmonton, 1989-90

For the second stage filtration, the effluent from the dual media filters was fed to the GAC contactors at two hydraulic loading rates. The results gave apparent first order rate constants varying from 0.022 to 0.043 min^{-1}. The x-intercept ranged from -2.0 to 5.4 µg/L, indicating a significantly lower value than in the first stage filtration. The correlation coefficients indicated good linearity, with coefficients varying from 0.94 to 0.99. The graphical relationship for GAC 4 is shown in Figure 20. All the correlation coefficients were significant at least at the 1% level. As with the dual media filtration, the apparent first-order rate constants appear to be dependent on hydraulic loading, where higher EBCTs yielded lower apparent rate constants. Therefore, there appeared to be little advantage to the longer EBCTs.

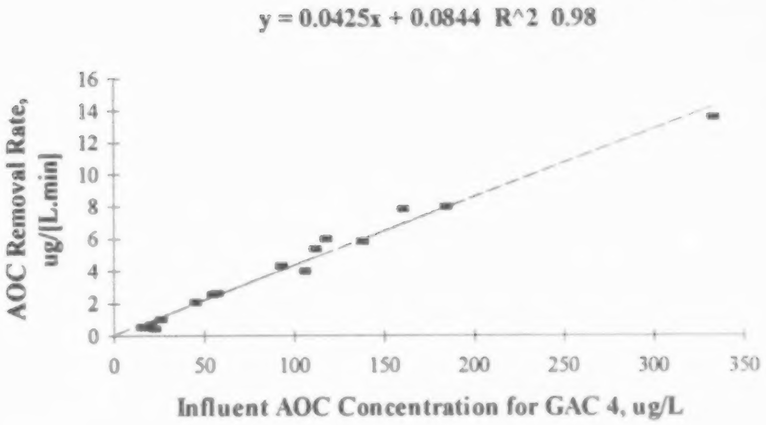


Figure 20 AOC Removal Rate vs. Influent Concentration for GAC 4, Edmonton, 1989-90

In general, there appeared to be some scatter in the data for the dual media filtration, and better linearity in the GAC contactors. The x-intercepts for all filters and GAC contactors were positive in all cases except one, indicating that there was a minimum concentration below which the biodegradable material could not be reduced biologically. It was observed that the higher x-intercepts were associated with the higher hydraulic loading streams.

Edmonton, Alberta 1992-1993

This Edmonton, Alberta study also reported AOC for influents and effluents for dual media filters and GAC contactors. The apparent first order rate constants and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercept was determined to obtain the minimum achievable concentration. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 14 and a graphical presentation for each filter and GAC contactor is displayed in Appendix B, Figures B9 to B10.

Table 14

AOC Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	-0.014 ± 0.09	54	0.758 ± 5.637	0.15‡	53-5.5
Filter 2	0.070 ± 0.105	31	-2.162 ± 6.979	0.60‡	5.5-6.1
Filter 3	0.081 ± 0.014	5.3	-0.432± 0.891	0.99	10.8-11.3
Filter 4	0.079± 0.023	16	-1.268 ± 1.356	0.97	8.8-15.7
Filter 5	0.105 ± 0.087	31	-3.205± 2.834	0.74†	5.9-5.5
GAC 2	0.046 ± 0.019	-4.6	0.213± 0.640	0.96	17.2-18.4
GAC 4	0.031 ± 0.015	27	-0.829 ± 0.587	0.91	34.5-42.7
GAC 5	0.034 ± 0.021	-2.8	0.094 ± 0.685	0.84	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals.

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, Filter 1 (chlorinated stream) yielded a negative apparent rate constant, -0.014 min^{-1}, and a low correlation coefficient which was not significant at the 5% level. The non-ozonated stream (Filter 5) was analyzed and an apparent rate constant of 0.105 min^{-1}, was determined to have a correlation coefficient significant at the 5% level. For the ozonated streams (Filters 2, 3 and 4), apparent rate constants ranged from 0.070 to 0.081 min^{-1}, and correlation coefficients ranged from 0.60 to 0.99. The coefficients were significant at the 1% level for Filter 3 and 4; however, a large amount of scatter was noted in Filter 2, specifically a number of negative removals. The graphical relationship for Filter 4 is shown in Figure 21. The x-intercepts ranged between 5.3 to 54 μg/L, where the higher x-intercepts were attributed to the higher hydraulic loading rates.

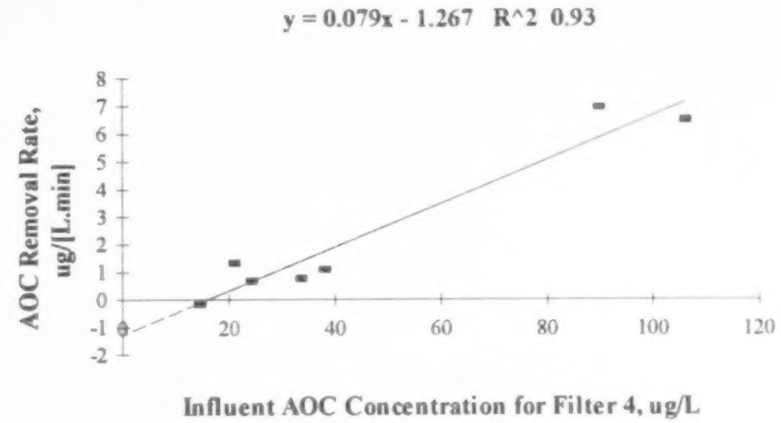


Figure 21 AOC Removal Rate vs. Influent Concentration for Filter 4 Edmonton, 1992-93

For the second stage filtration, the GAC contactors were hydraulically loaded at two rates. GAC 3 was not analyzed since very few data points were available. The results gave apparent first order rate constants varying from 0.031 to 0.046 min^{-1}. All the GAC contactors showed good linearity, and all correlation coefficients were significant at least at the 1% level. The graphical relationship for GAC 2 is shown in Figure 22. The Pica carbon (GAC 4) had the lowest apparent rate constant and GAC 2 had the highest apparent rate constant. These results correspond to the same trend noticed in the NVOC analysis. It would also appear that the apparent rate constants were dependent on hydraulic loading rate, where higher EBCT contactors show little removal in the lower portion of the bed. The x-intercept ranged between -4.6 and 27 μg/L, indicating some uncertainty in the minimum concentration to which the biodegradable material could be reduced biologically. Realistically, all AOC could not be eliminated biologically.

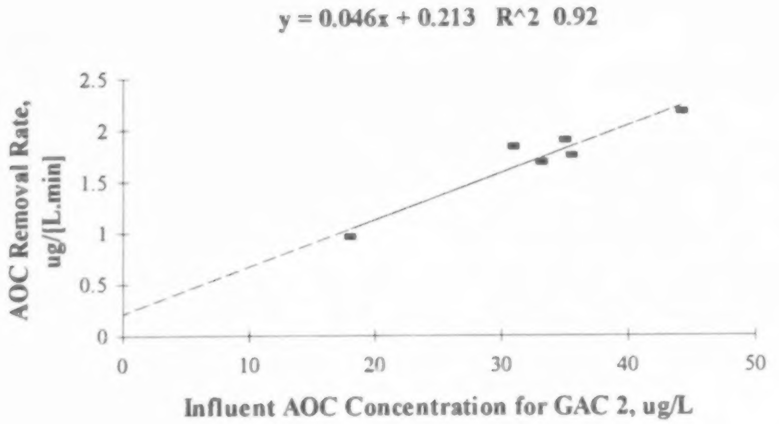


Figure 22 AOC Removal Rate vs. Influent Concentration for GAC 2 Edmonton, 1992-93

Laval, Quebec

The Laval, Quebec study measured AOC, according to the procedure described by van der Kooij (1982, 1984), with minor modifications. Although slightly different modifications were used for the Edmonton studies, the Laval method could be considered similar when comparing results from the Edmonton, Alberta study to the Laval study. Adequate data were not available for the dual media filtration, however data for two BAC contactors were available in addition to profile data. Figures 23 and 24 display the graphical analysis for the two contactors. Table 15 summarizes the apparent rate constants, and y-intercepts with their 95% confidence intervals. The x-intercepts were determined and the correlation coefficient were calculated and their level of significance determined.

Table 15
AOC Summary for Laval, Quebec Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
BAC 2G 10 cm	0.162 ± 0.214	140	-22.65 ± 41.08	0.66‡	5.0-7.0
BAC 2G 70 cm	0.034 ± 0.072	118	-3.997 ± 13.29	0.48‡	13.0-16.0
BAC 2G 130 cm	0.024 ± 0.020	61	-1.474 ± 3.885	0.81‡	20.0-26.0
BAC 2G Effluent	0.024 ± 0.018	57	-1.359 ± 3.543	0.84†	28.0-36.0
BAC 5D 15 cm	0.163 ± 0.733	174	-28.30 ± 132.5	0.56‡	5.0-6.0
BAC 5D 80 cm	0.061 ± 0.095	106	-6.472 ± 17.13	0.89‡	13.0-16.0
BAC 5D 140 cm	0.022± 0.046	84	-1.843± 8.325	0.82‡	20.0-26.0
BAC 5D Effluent	0.031 ± 0.011	81	-2.518 ± 2.229	0.97	28.0-36.0

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

The second stage filtration employed a prior ozonation step and a design hydraulic loading rate of 4 m/h. Individual EBCTs for each sampling day were obtained and used in the calculations. The results for the two BAC contactors analyzed gave apparent first order rate constants of 0.024 and 0.031 min^{-1}. The correlation coefficient for BAC 2G was significant at the 5% level and the correlation coefficient for BAC 5D was significant at the 1% level.

Apparent rate constants were determined for three locations along the depth of these contactors. The rate constants averaged 0.163 min^{-1} for a depth of 12.5 cm, 0.048 min^{-1} for a depth of 75 cm, and 0.023 min^{-1} for depth of 135 cm. These profile results had correlation coefficients not significant at the 5% level; however, similar trends through the depth of the contactor were observed as with the NVOC profiles. These result indicate a greater removal rate near the top of the contactors with decreasing removal rates with depth in the contactor. The x-intercepts were significantly higher near the top of the bed and decreased with depth. The effluents from these two BAC contactors resulted in x-intercepts of 56.6 and 81.2 μg/L.

Although correlation coefficients not significant at the 5% level were found along the depth of the column, the average apparent rate constants corresponded very closely to the Laval NVOC rate constants. It was also noted that the apparent rate constants did not decrease after the 135 cm depth indicating no further change in substrate composition.

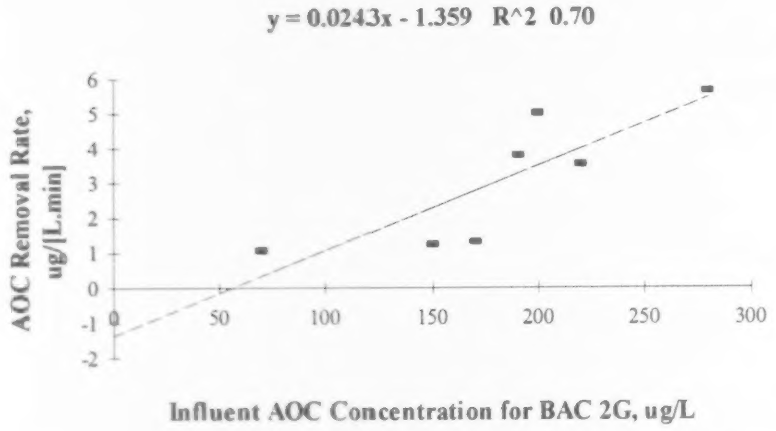


Figure 23: AOC Removal Rate vs. Influent Concentration for BAC 2G, Laval, Quebec Study

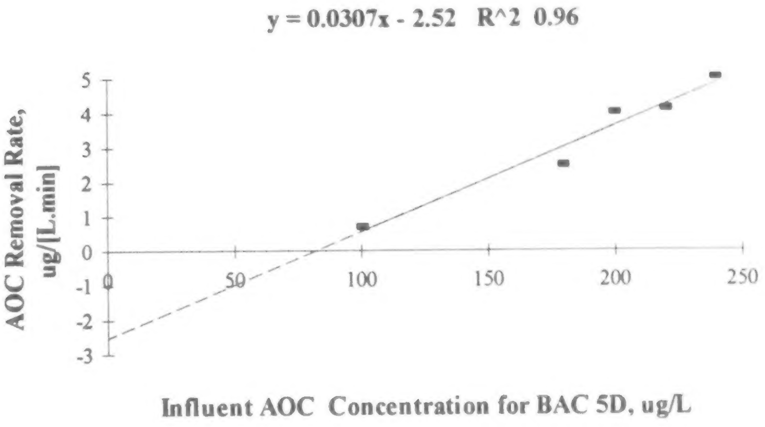


Figure 24: AOC Removal Rate vs. Influent Concentration for BAC 5D, Laval, Quebec Study

Figure 25 displays a profile of the apparent rate constants for selected segments in the depth of the contactors. All of the data collected along the depth of the contactors produced correlation coefficients not significant at the 5% level, accept for the 130 cm for BAC 2G and the 200 cm depth in BAC 5D. Although the first order relationship for these data is not statistically significant it would appear that the same trends noted in the TOC profile may also exist for AOC. The noted trends indicate that a higher apparent rate constant occurs near the top of the contactor and decreases with depth.

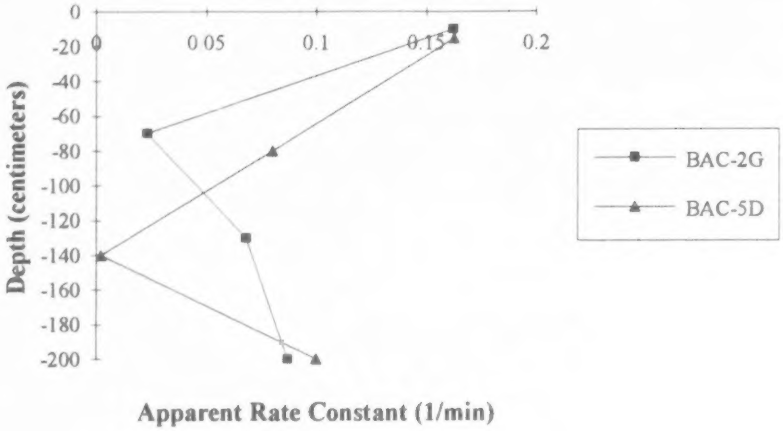


Figure 25: AOC Apparent Rate Constant Profile for BAC 2G and 5D, Laval, Quebec Study

Cincinnati, Ohio

The Cincinnati Study determined AOC for influent and effluent locations for eight dual media filters. This study only employed one stage of filtration and each filter contained, either anthracite and sand, sand only, or GAC and sand. The AOC reported in this study was given only in the form of AOC-NOX calculated in units of C eq of oxalate. The experimental protocol was that described by van der Kooij (1982,1987).

The data from the eight dual media filters were analyzed and apparent first-order rate constants and y-intercepts were calculated with their 95% confidence intervals. These results are summarized in Table 16 along with correlation coefficients and x-intercepts. A graphical presentation of the analysis is displayed in Appendix B, Figure B12 to B14.

Table 16

AOC Summary for Cincinnati, Ohio Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.048 ± 0.021	474	-22.76 ± 7.696	0.71	10.32
Filter 2	0.066 ± 0.021	181	-11.92 ± 7.711	0.82	10.43
Filter 3	0.084 ± 0.012	156	-13.08 ± 4.289	0.95	9.82
Filter 4	0.083 ± 0.008	147	-12.27 ± 2.924	0.98	10.47
Filter 5	0.078 ± 0.011	142	-11.09 ± 3.939	0.96	10.04
Filter 6	0.074 ± 0.012	72	-5.312 ± 3.852	0.95	11.49
Filter 7	0.074 ± 0.012	95	-7.001± 4.326	0.94	11.26
Filter 8	0.079 ± 0.010	123	-9.713 ± 3.567	0.96	10.29

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals.

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For this first and only stage of filtration, the filters were hydraulically loaded at the same rate (5 m/h), and all filters received the same pre-treatment, being ozonation of the raw water and subsequent coagulation and sedimentation. Filter 1 was a chlorinated anthracite and sand filter and resulted in a lower correlation coefficient; however, it was still significant at the 1% level, since many data points were obtained. The apparent rate constant was lower than other filter and was determined to be 0.048 min^{-1}. Filter 2 was an anthracite sand filter but was backwashed with chlorinated water. This combination resulted in a higher apparent rate constant than Filter 1 and better linearity. The remaining six filters yielded apparent rate constants ranging from 0.074 to 0.084 min^{-1} with correlation coefficients ranging from 0.94 to 0.98. The GAC/sand filters produced apparent rate constants slightly lower than the anthracite/sand filters. The filters all show excellent linearity and the relationships were all significant at the 1% level. The graphical relationship is displayed for Filters 4 and 8 in Figure 26 and 27 respectively. The x-intercepts ranged between 72 and 474 μg/L. Although these values appear to be very large it should be noted that the AOC for this study was only reported for AOC-NOX in units of oxalate equivalents. This study also reported AOC-P17 for two filters, which when analyzed produced correlation coefficients not significant at the 5% level. These results can be found in Appendix B, Figure B14.

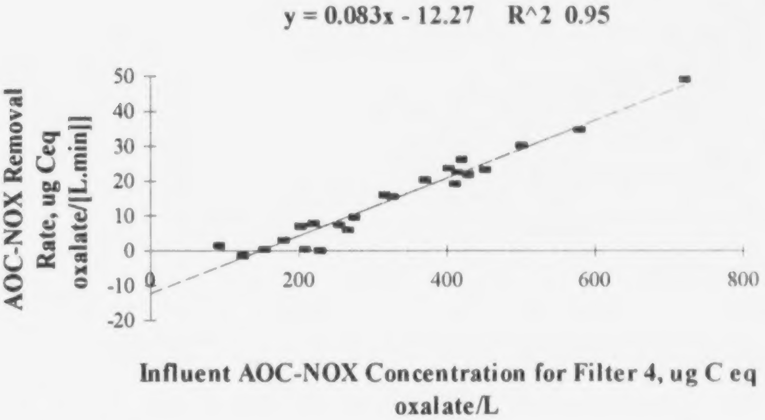


Figure 26: AOC Removal Rate vs. Influent Concentration for Filter 4, Cincinnati, Ohio Study

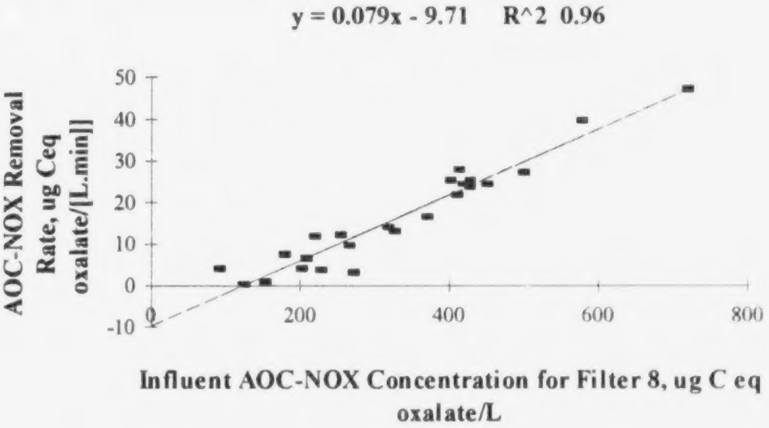


Figure 27: AOC Removal Rate vs. Influent Concentration for Filter 8, Cincinnati, Ohio Study

Woodbridge, CT

The Woodbridge study reported AOC, as AOC-NOX, AOC-P17 and total AOC. As noted in the NVOC section it was unfortunate that during the study the hydraulic loading rate was doubled for two sampling days, and only a total of five sampling events were analyzed. The apparent rate constants were calculated with their 95% confidence intervals for each stream. The correlation coefficients were determined and their level of significance noted. The results were extremely poor and no relationships were apparent for any of the filters, perhaps as a results of the significant changes in hydraulic loading rate. These changes could create non-steady state biofilm conditions. It was decided at this stage to attempt to analyze the data using the lower hydraulic loading rate despite the indication that this rate was changed throughout the study. After the re-analysis of the data using the same hydraulic loading rate a better relationship was apparent. The results for filter 1, total AOC for Filter 1, the ozonated, GAC/sand filter are displayed in Figure 28. The results for the remaining filters are graphically displayed in Appendix B, Figure B15. Table 17 summaries the results for total AOC when the same hydraulic loading was used in the analysis.

Table 17

AOC Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.078 ± 0.060	18	-1.433 ± 5.814	0.95†	6.2-12.2
Filter 2	0.059 ± 0.133	15	-0.889 ± 12.66	0.80‡	6.2-12.2
Filter 3	0.030 ± 0.670	1.9	-0.578 ± 34.49	0.13‡	6.2-12.2
Filter 4	0.400 ± 2.457	46	-18.27 ± 129.3	0.44‡	6.2-12.2
Filter 5	-0.34 ± 5.196	59	20.19 ± 253.2	0.20‡	6.2-12.2

Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

The results for total AOC for Filter 1 gave an apparent rate constant of 0.078 min^{-1}, and a correlation coefficient of 0.95, which was significant at the 5% level. The x-intercept for filter 1 was 18 µg/L, indicating a minimum concentration which cannot be further reduced biologically. The other four filters which consisted of both GAC and anthracite filters, with combinations of ozonation, non-ozonation and backwashing with chlorinated water, produced very poor results. Although these data are not useful to compare with other studies, they are helpful to confirm that the AOC data are dependent on hydraulic loading rate, and that first order analysis is not possible unless relatively constant hydraulic loading rates are employed.

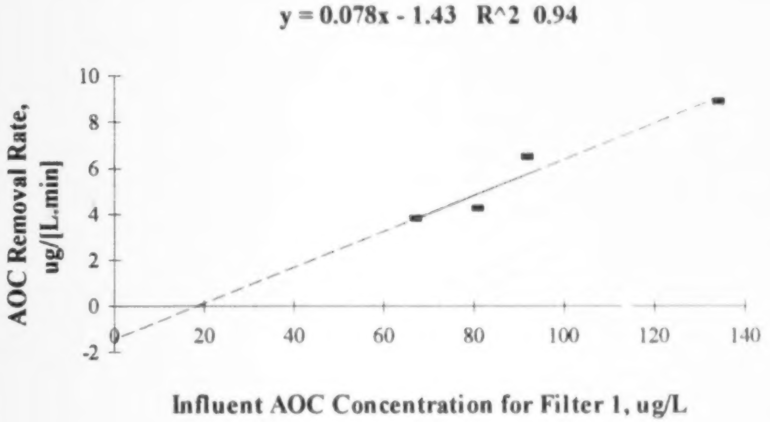


Figure 28: AOC-Total Removal Rate vs. Influent Concentration for Filter 1, Woodbridge, CT Study

Discussion and Comparison for AOC

In an attempt to discuss and compare the AOC results for all the studies, two graphs were generated. Figure 29 displays the calculated apparent rate constants versus the EBCT and Figure 30 indicates the minimum achievable AOC concentration versus EBCT. These figures were generated using only apparent rate constants for streams showing significant linearity. In general it appeared that non-chlorinated and pre-ozonated streams exhibited better linearity than non-ozonated and chlorinated streams. It was also noted that chlorinated stream or streams backwashed with chlorinated water which were linearly significant, produced lower apparent rate constants than non chlorinated stream. Therefore, chlorine had decreased the removal of AOC in a stream.

The Woodbridge results were not used in Figure 29 since the EBCT changed significantly throughout the study. When the apparent rate constants from four studies were plotted against their average operating EBCT, a distinct non-linear relationship was observed. This occurred despite the different waters, media type, and operating conditions among studies. The Cincinnati results were included since the apparent rate constants were independent of the AOC units used (oxalate in this case); however, the present investigation only analyzed AOXFP-NOX and not total AOC. It would therefore be expected that AOC-NOX would produce a slightly different curve. It is interesting to note that the EBCT for the Cincinnati study appear to occur close to the steepest point in this non-linear relationship. This plot also demonstrates that there appears to be little advantage to operate at EBCTs greater than approximately 25 minutes, since the curve flattens indicating the lowest achievable apparent rate constant for AOC.

Although most of the cumulative apparent rate constants determined for the Laval study along the depth of the column were not linearly significant, the same relationship observed in Figure 29 was seen along the depth of all the columns.

The AOC apparent rate constant decreases with increasing EBCT, because of the influence of two factors. Because AOC includes a mix of substrates with different biodegradation kinetics, a longer EBCT allow some substrates with slower kinetics to be biodegraded, leading to a lower overall rate constant for the entire reactor. In addition, because all filters had approximately the same depth of media, a shorter EBCT corresponds to a higher hydraulic loading, and therefore to a higher substrate flux (J).

Biofilm kinetics states that as J increases, the amount of biomass increases, and therefore the capacity of the reactor to remove substrate increases.

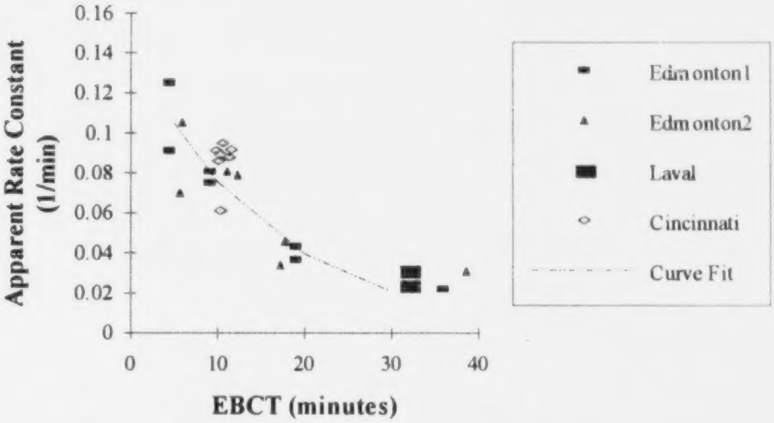


Figure 29: AOC Apparent Rate Constant vs. EBCT

The agreement of the data among studies is very good, and this observation could lead to a design relationship. To better define the non-linear relationship, several equation forms were employed to fit the curve. An equation in the form $x = ae^{-by}$ was found to best define the relationship. The equations were developed through a trial and error process, and a Least Squares analysis was not performed. This curve fit only intended to provide a semi-quantitative basis for comparision. The equation for AOC apparent rate constants and EBCT is:

$$\text{EBCT} = 0.145 \times e^{-(0.065 \times \text{AOC apparent rate constant})}$$

The x-intercept was also plotted against EBCT (Figure 30), and no apparent relationship was observed, although it was noted that in some studies the x-intercept appeared to decrease with increasing EBCT. Generally the x-intercept decreases at the second filtration stage for linearly significant streams, however not always. The Cincinnati study was not included in the figure, since the units were different than the other studies. Again the Laval study indicated a higher minimum achievable AOC concentration. The influent AOC concentrations ranged from 70 to 280 μg/L (eq C as acetate). The AOC influent for the GAC contactors for the combined Edmonton studies ranged from 0 to 130 μg/L (eq C as acetate). Therefore, the higher x-intercepts could be attributed to a higher range of influent AOC or more extreme temperatures.

Figure 30 also suggests an EBCT in which there is no further decrease in S_{min} (x-intercept). The Edmonton data suggest anything more than 10 minutes will not produce lower AOC concentrations. The minimum x-intercept value achieved at this EBCT is approximately 7 μg/L (eq C as acetate).

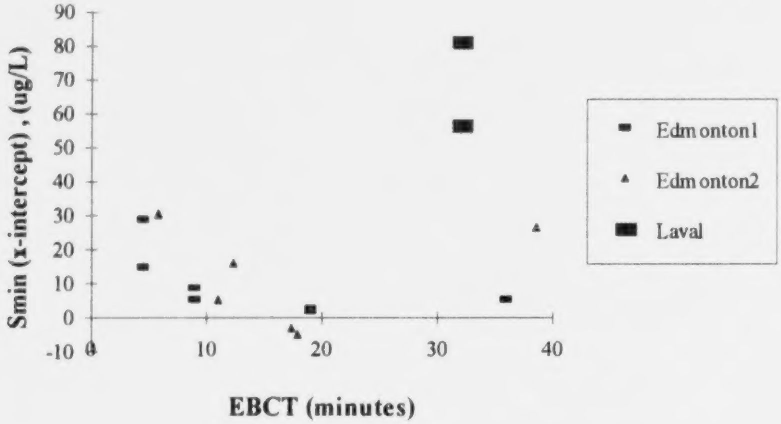


Figure 30: Minimum Achievable AOC Concentration vs. EBCT

The results presented above for Edmonton are based on apparent rate constants and x-intercepts that have been calculated for two separate filtration processes (first and second stage filtration). The influent to the second stage has therefore alreading had the most easily beodegradable material removed. It is noted that these calculations could be repeated using the total EBCT for the two filtration processes and therefore effectively represent only one filtration step (two filtration steps in series).

5.3 Biodegradable Organic Carbon

Laval, Quebec

The Laval, Quebec study measured BDOC according to the procedure described by Servais et al, (1987), which is described in Section 3.3. Although this parameter was not measured in any other study it is useful to compare to the BOM parameters. Adequate data were not available for the dual media filtration, however data for the two BAC contactors were available in addition to profile data. Figures 31 and 32 display the graphical analysis for the two contactor. Table 18 summarizes the apparent rate constants, and y-intercepts with their 95% confidence intervals. The x-intercepts were determined to obtain a minimum achievable concentration. The correlation coefficients were calculated and their level of significance determined.

Table 18
BDOC Summary of Laval, Quebec Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
BAC 2G 10 cm	0.100 ± 0.081	229	-22.87 ± 42.71	0.82†	5.0-7.0
BAC 2G 70 cm	0.032 ± 0.040	-105	3.348 ± 20.99	0.67‡	13.0-16.0
BAC 2G 130 cm	0.024 ± 0.023	122	-2.920 ± 12.02	0.77†	20.0-26.0
BAC 2G Effluent	0.025 ± 0.015	114	-2.838 ± 7.673	0.89	28.0-36.0
BAC 5D 15 cm	0.014 ± 0.153	-994	13.91 ± 72.32	0.17‡	5.0-6.0
BAC 5D 80 cm	0.025 ± 0.118	-35	0.872 ± 59.64	0.53‡	13.0-16.0
BAC 5D 140 cm	0.016± 0.043	-246	3.932± 20.42	0.55‡	20.0-26.0
BAC 5D Effluent	0.017 ± 0.017	-121	2.052 ± 11.13	0.81‡	28.0-36.0

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5%

The second stage filtration employed a prior ozonation step and a design hydraulic loading rate of 4 m/h. Individual EBCTs for each sampling day were obtained and used in the calculation. The results for the two BAC contactor analyzed gave apparent first order rate constant of 0.017 and 0.025 min^{-1}. The correlation coefficient for BAC 2G was significant at the 1% level; however, the correlation coefficient for GAC 5D was not significant at the 5% level. This may be due in part to the fact that only four data points were available for this contactor. Apparent rate constants were determined for three locations along the depth of these contactors. The results for BAC 5D were inconsistent for all locations sampled and yielded correlation coefficients which were not significant at the 5% level. The x-intercepts were negative at all sample locations. For the effluent location of BAC-2G, the x-intercept was 114 μg/L and this was the only set of data giving a correlation coefficient significant at the 1% level.

The rate constants for BAC 2G were 0.100 min^{-1} for a depth of 10 cm, 0.032 min^{-1} for a depth of 70 cm, and 0.024 min^{-1} for depth of 130 cm. These profile results had correlation coefficients significant at the 5% level, except for the 70 cm depth. It was noted that similar trends through the depth of the contactor were observed as with the NVOC and AOC profiles. These result indicated a greater removal rate near the top of the contactors with decreasing removal rates with depth in the contactor as would be expected. It was also noted as with the AOC parameter that the apparent rate constants did not decrease after the 140 cm depth, indicating no further change in substrate composition.

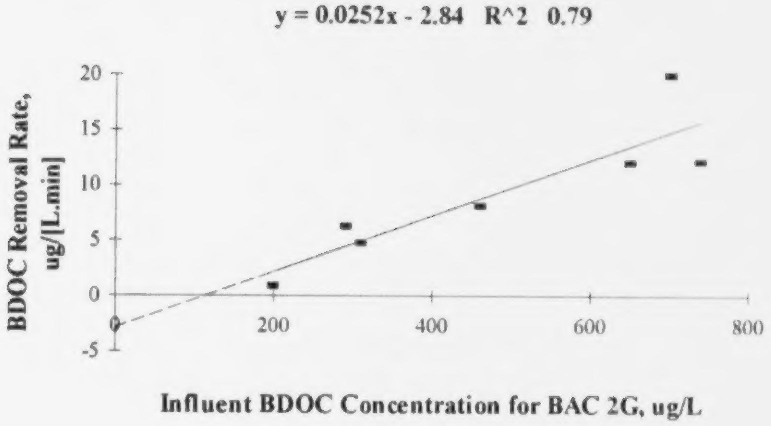


Figure 31: BDOC Removal Rate vs. Influent Concentration for BAC 2G, Laval, Quebec Study

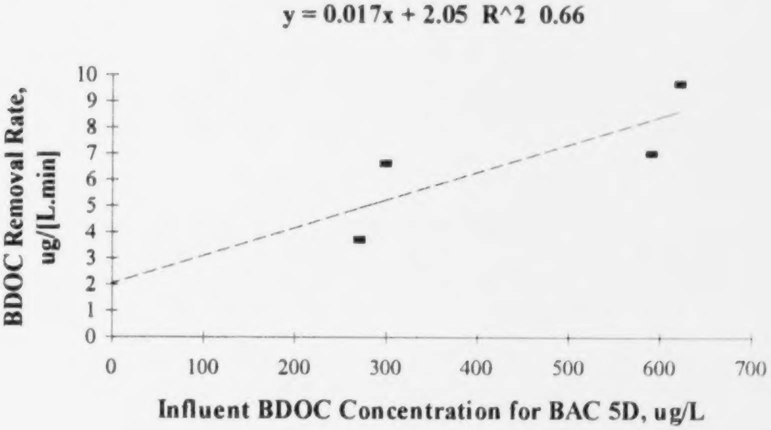


Figure 32: BDOC Removal Rate vs. Influent Concentration for BAC 5D, Laval, Quebec Study

Figure 33 displays a profile of the apparent rate constants for individual segments along the depth of the contactor. Most of these sample points produced correlation coefficients not significant at the 5% level except for the effluent location for BAC 2G. The profile indicated both increasing and decreasing apparent rate constants throughout the depth of the contactors, with higher rate constants for BAC 2G.

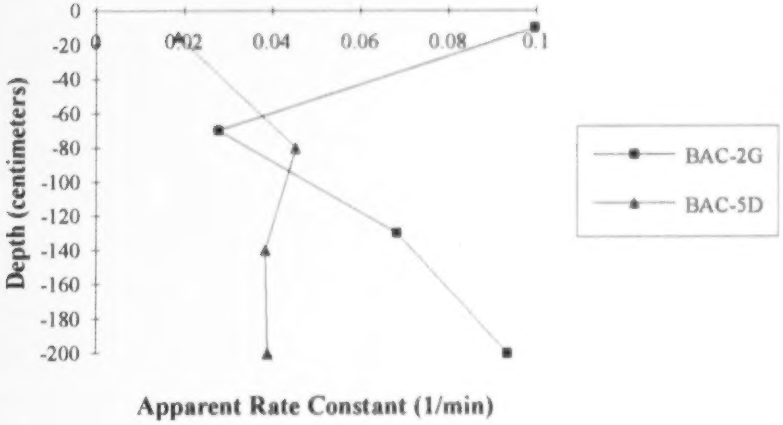


Figure 33: BDOC Apparent Rate Constant Profile for BAC 2G and 5D, Laval, Quebec Study

The parameter BDOC was not available for any other study, and unfortunately for most of the results from Laval the correlation coefficient for the rate constant was not statistically significant. From the data available from Laval it would be expected that the BDOC parameter would produce a similar apparent rate constant versus EBCT relationship as was observed for the AOC data.

5.4 Haloacetic Acid Formation Potential (HAAFP)

HAAFP refers to precursors of haloacetic acids. The more commonly reported parameters are dichloroacetic acid formation potential (DCAAFP) and trichloroacetic acid formation potential (TCAAFP). These parameters were available for the Edmonton (1992-1993), Cincinnati and Woodbridge studies.

5.4.1 Dichloroacetic Acid Formation Potential (DCAAFP).

Edmonton, Alberta, 1992-1993

The Edmonton, Alberta study reported DCAAFP for influents and effluents of dual media filters and GAC contactors. The apparent first order rate constants, and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercepts were calculated to estimate the minimal achievable concentration. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 19 and a graphical presentation for each filter and GAC contactor is displayed in Appendix B, Figures B16 and B17.

Table 19

DCAAFP Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (μg/L)	y-intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.037± 0.091	6.6	-0.243 ± 2.888	0.29‡	5.3-5.5
Filter 2	0.159 ± 0.041	13	-2.010 ± 1.169	0.95	5.5-6.1
Filter 3	0.068 ± 0.055	9.4	-0.635 ± 1.142	0.87†	10.8-11.3
Filter 4	0.052 ± 0.011	1.4	-0.075 ± 0.337	0.96	8.8-15.7
Filter 5	0.093± 0.055	7.2	-0.665 ± 1.898	0.81	5.9-5.5
GAC 2	0.050 ± 0.061	0.90	-0.047 ± 0.211	0.94	17.2-18.4
GAC 3	0.024 ± 0.013	2.7	-0.065 ± 0.200	0.90	34.5-38.1
GAC 4	0.024 ± 0.003	2.1	-0.050 ± 0.036	0.99	34.5-42.7
GAC 5	0.059 ± 0.008	4.3	-0.253 ± 0.150	0.99	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, filter 5 (non-ozonated stream) produced an apparent rate constant of 0.093 min^{-1} and a correlation coefficient of 0.81 was determined to be significant at the 1% level. The chlorinated stream (Filter 1) was determined to have an apparent first order rate constant of 0.037 min^{-1} and a correlation coefficient of 0.29 which was not significant at the 5% level. The calculated apparent rate constants for the ozonated streams ranged from 0.052 to 0.16 min^{-1} and correlation coefficients ranged from 0.87 to 0.96. The correlation coefficient for Filter 3 was not significant at the 1% level but significant at the 5% level. The x-intercept ranged between 1.4 and 13.0 μg/L indicating a wide range of the minimal achievable concentration. The results for these filters showed a fairly good linear pattern, and Filter 4 (filter adsorber stream) showed a good relationship. The apparent rate constants appeared to vary according to the hydraulic loading rate (Figure 34). In addition, it was observed that the ozonated stream 2, produced a higher apparent rate constant then the non-ozonated stream 5. However, further comparison of these streams reveal that the x-intercept for Filter 2 was higher than Filter 5.

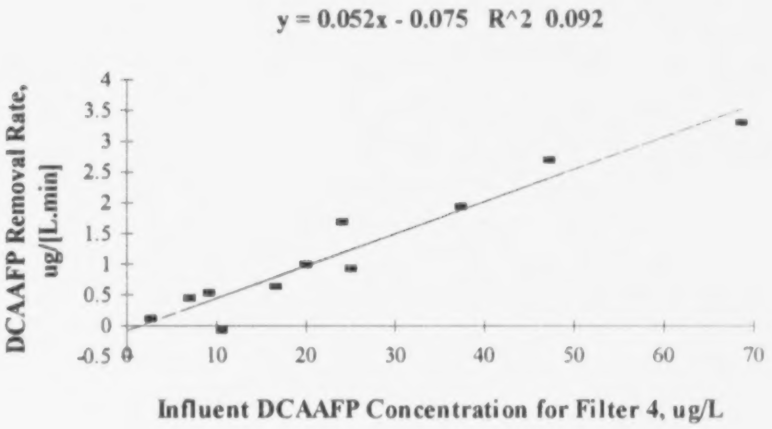


Figure 34: DCAAFP Removal Rate vs. Influent Concentration for Filter 4, Edmonton, 1992-93 Study

For the second stage filtration, the GAC contactors were hydraulically loaded at two rates. The results gave apparent first order rate constants varying from 0.024 to 0.059 min^{-1}. The x-intercept ranged between 0.94 to 4.3 μg/L indicating a lower minimum achievable concentration level than the first stage filtration. All the GAC contactors showed good linearity, and all correlation coefficients were significant at least at the 1% level. GAC 2 had the lowest x-intercept and the non-ozonated stream (GAC 5) had the highest x-intercept. The linear relationship for GAC 5 is displayed in Figure 35.

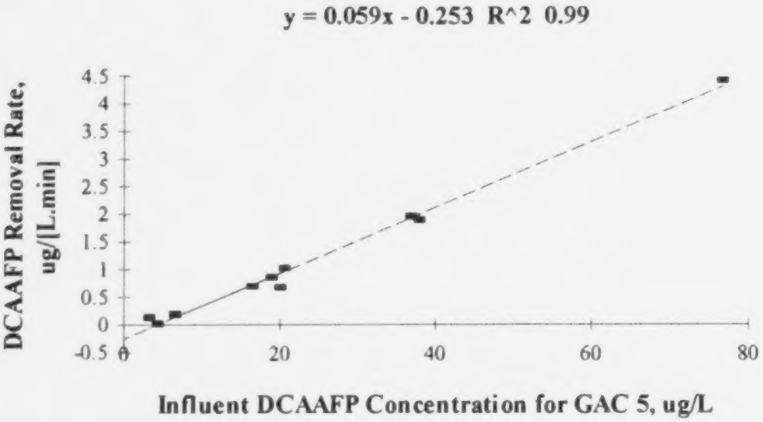


Figure 35: DCAAFP Removal Rate vs. Influent Concentration for GAC 5, Edmonton, 1992-93 Study

In general it would appear that during both first and second stage filtration, the apparent first order rate constant was dependent on hydraulic loading rate. Therefore, the higher EBCTs would typically show lower apparent rate constants. These results indicate that little removal was achieved in the lower portion of the bed for the low hydraulic loading rate. The y-intercept for the filters and GAC contactors was negative in all cases, although most of the 95% confidence intervals included zero. A negative y-intercept leads to be positive x-intercept, indicating a minimum concentration below which the biodegradable material could not be reduced biologically. These data therefore suggest such a minimum concentration, but that value is quite low.

Table 20 displays the results from a profile of DCAAFP concentrations at various positions in Streams 2 and 4 during a spring run-off event. The data for these streams where obtained on different days. For stream 2, both the cumulative and segment apparent rate constants included some negative values for the filters. In GAC 2, the apparent rate constants decreased with depth. For stream 4, the apparent rate constants in the filter show a decrease with depth for the cumulative rate constants and a negative value for the segment rate constants. In GAC 4, a sharper decrease with depth for both cumulative and segment apparent rate constants was noted. It is felt that the sharper decrease in apparent rate constant was a result of stream 4 containing the filter adsorber for its first stage filtration step. In general, stream 2 (low EBCT) showed higher apparent rate constants than with stream 4 (higher EBCT), which was consistent with what was observed in the above analysis. The segment apparent rate constants are graphically displayed in Figure 36.

Table 20

Profile DCAAFP Results for Streams 2 and 4

Location	DCAAFP (μg/L)	Segment Apparent Rate Constants (min^{-1})	Cumulative Apparent rate Constants (min^{-1})
Following Ozonation	9.96		
Filter 2-31cm	17.36	-0.381	-0.381
Filter 2-61cm	16.58	-0.173	0.024
Filter 2-91 cm	18.65	-0.153	-0.066
GAC 2-10 cm	17.17	0.106	0.106
GAC 2-47 cm	12.64	0.092	0.094
GAC 2-230 cm	2.79	0.049	0.057
Following Ozonation	25.08		
Filter 4-31cm	12.36	0.132	0.132
Filter 4-62 cm	14.17	0.057	-0.038
Filter 4-91 cm	14.57	0.037	-0.007
GAC 4-23 cm	9.45	0.100	0.100
GAC 4-47 cm	9.12	0.052	0.009
GAC 4-230 cm	4.49	0.020	0.018

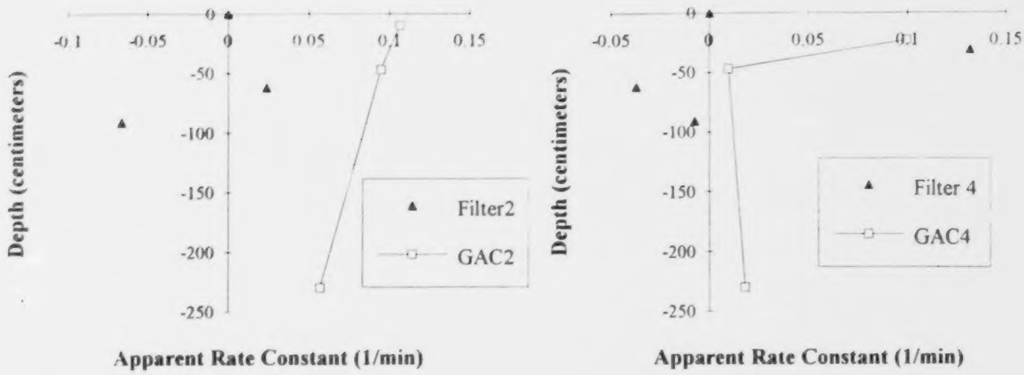


Figure 36: DCAAFP Apparent Rate Constant Profile for Streams 2 and 4, Edmonton, Alberta, 1992-1993

Cincinnati, Ohio Study

The Cincinnati study determined DCAAFP for influent and effluent locations of eight dual media filters. This study only employed one stage of filtration and each filter contained either anthracite and sand, sand or GAC and sand. The analytical protocol was described as being taken from Standard Methods or EPA Methods.

The data from the eight dual media filters were analyzed and apparent first-order rate constants and y-intercepts were calculated with their 95% confidence intervals. These results are summarized in Table 21 along with correlation coefficients and their significance levels. The x-intercept were also determined to obtain the minimum achievable concentration . A graphical presentation of the analysis is displayed in Appendix B, Figure B18 and B19.

Table 21

DCAAFP Summary for Cincinnati, Ohio Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.026 ± 0.017	28	-0.732 ± 0.656	0.58	10.32
Filter 2	0.024 ± 0.022	-2.5	0.059 ± 0.779	0.46†	10.43
Filter 3	0.035 ± 0.013	-4.1	0.144 ± 0.494	0.74	9.82
Filter 4	0.036 ± 0.014	-3.9	0.140 ± 0.495	0.75	10.47
Filter 5	0.032 ± 0.013	-6.2	0.196 ± 0.458	0.75	10.04
Filter 6	0.078 ± 0.023	1.1	-0.082 ± 0.846	0.81	11.49
Filter 7	0.069 ± 0.025	3.8	-0.259 ± 0.868	0.80	11.26
Filter 8	0.038 ± 0.009	-7.9	0.301 ± 0.313	0.89	10.29

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For this first and only stage of filtration, the filters were hydraulically loaded at the same rate (5 m/h) and all filters received the same pre-treatment. Filter 1 was a chlorinated anthracite and sand filter and resulted in a correlation coefficient of 0.026 min^{-1}, and the highest x-intercept (28 μg/L). This filter resulted in a correlation coefficient significant at the 1% level, since many data points were obtained. Filter 2 was an anthracite sand filter but was backwashed with chlorinated water. This combination resulted in a low apparent rate constants (0.024 min^{-1}) as seen in Filter 1; however, the correlation coefficient was only significant at the 5% level. The two other anthracite-sand filters and the sand filter (Filters 3, 4 and 5) yielded apparent rate constants ranging from 0.032 to 0.036 min^{-1}, with correlation coefficients ranging from 0.74 to 0.75. These filters all showed better linearity than the chlorinated filters and all correlations were significant at the 1% level. The relationship is shown in Figure 37 for Filter 3.

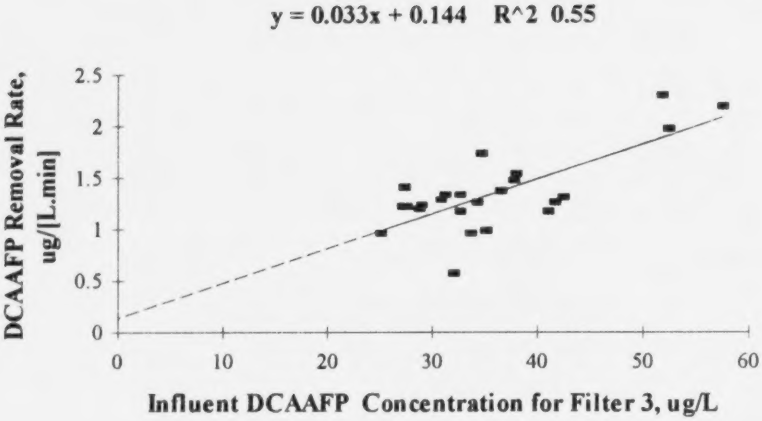


Figure 37: DCAAFP Removal Rate vs. Influent Concentration for Filter 3, Cincinnati, Ohio Study

For the GAC/sand filter (6, 7 and 8), a range of apparent rate constants was obtained. They ranged between 0.038 to 0.078 min^{-1}, and all correlation coefficients were significant at the 1% level. The graphical relationship for Filter 8 is shown in Figure 37. It was also noted that both positive and negative x-intercepts were determined, however all values were low.

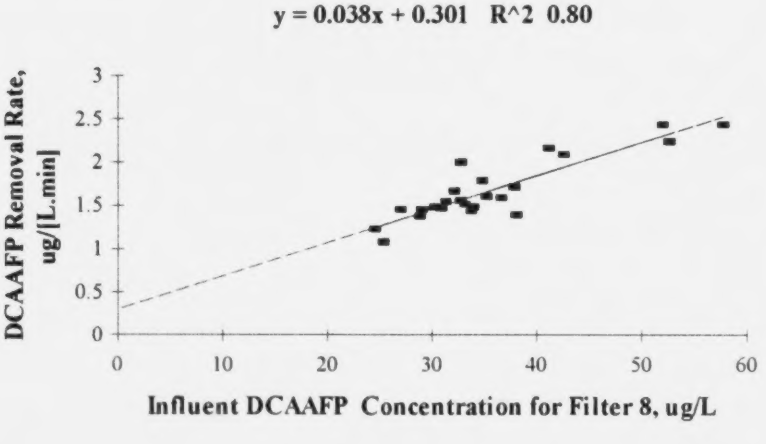


Figure 38: DCAAFP Removal Rate vs. Influent Concentration for Filter 8, Cincinnati, Ohio Study

Woodbridge, CT

The Woodbridge study reported DCAAFP for influent and effluent locations for five filters. As noted in the above sections it was unfortunate that during the study the hydraulic loading rate was doubled for two sampling days, and only a total of five sampling events were analyzed. The apparent rate constants were calculated with their 95% confidence intervals for each stream. The correlation coefficients were determined and their level of significance noted. It was noted at this point in the analysis that the results were extremely poor and no relationships were apparent for any of the filters. It was decided at this stage to attempt to analyze the data using the lower hydraulic loading rate despite the indication that the flowrate was changed during the study. This attempt resulted in slightly better results, however none of the correlation coefficients were significant at the 5% level. It was decided not to use this data for comparison; however, the graphical presentation of this data can be found in Appendix B, Figure 20.

Discussion and Comparison of DCAAFP

In an attempt to discuss and compare the DCAAFP results for all the studies, two graphs were generated. Figure 39 displays the calculated apparent rate constants versus the EBCT and Figure 40 indicates the minimum achievable DCAAFP concentration versus EBCT. These figures were generated only using apparent rate constants for streams showing significant linearity. In general it appeared that chlorinated and chlorinated backwashed stream exhibited poor linearity and lower apparent rate constants than ozonated streams. The first stage filtration indicated good linearity, and better linearity was observed in the second stage filtration. As with the AOC data it was observed that the apparent rate constants were dependent on EBCT. This relationship is shown in Figure 39, using only the data from the Edmonton and Cincinnati studies. The Edmonton study clearly indicates a non-linear relationship between the apparent rate constant and EBCT. The Cincinnati study was operated at approximately the same EBCT for all streams. The points which fall along the Edmonton curve were filters with GAC/sand, whereas the points below the curve represent filters with anthracite/sand and sand. In addition, two of these streams below the curve were chlorinated.

To better define the non-linear relationship, several equation forms were employed to fit the curve. An equation in the form $x = ae^{-by}$ was found to best define the relationship. The equations were developed through a trial and error process, and a Least Squares analysis was not performed. This curve fit only intended to provide a semi-quantitative basis for comparision. The equation for DCAAFP apparent rate constants and EBCT is:

$$\text{EBCT} = 0.220 \times e^{-(0.08 \times \text{DCAAFP apparent rate constant})}$$

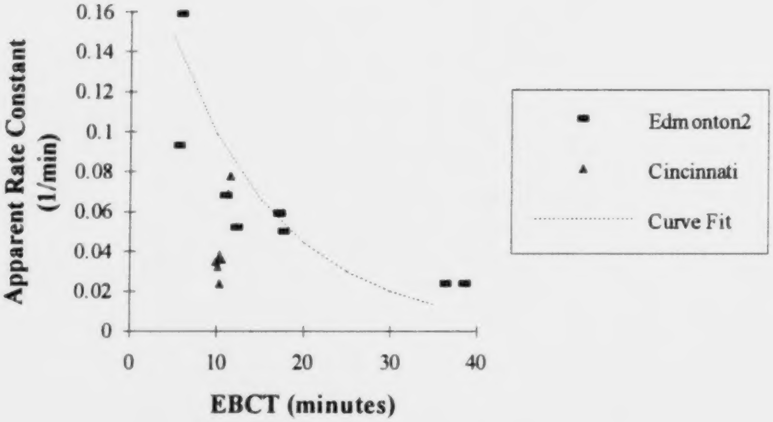


Figure 39: DCAAFP Apparent Rate Constant vs. EBCT

The x-intercept was also plotted against the EBCT (Figure 40). For the Edmonton study, there would appear to be a relationship, indicating that the x-intercept decreased with EBCT. Although this relationship could only be expressed qualitatively, in general it was observed that the x-intercept was lower at the second stage filtration. Therefore, it would appear that the x-intercepts for the Cincinnati study remain lower than the Edmonton study. The range of DCAAFP influent concentrations for Cincinnati was 1.4 to 47.9 μ g/L. The range experienced for the Edmonton study was 2.61 to 80.4 μg/L. It could then be argued that higher x-intercepts appear to be related to higher influent concentrations. The Cincinnati study also operated at higher water temperatures.

Figure 40 suggest an EBCT in which there is no further decrease in S_{min} (x-intercept). The Edmonton data suggest that anything more than 15 minutes will not produce lower

DCAAFP concentrations. The minimum x-intercept value achieved at 15 minutes is approximately 3 µg/L for the Edmonton study.

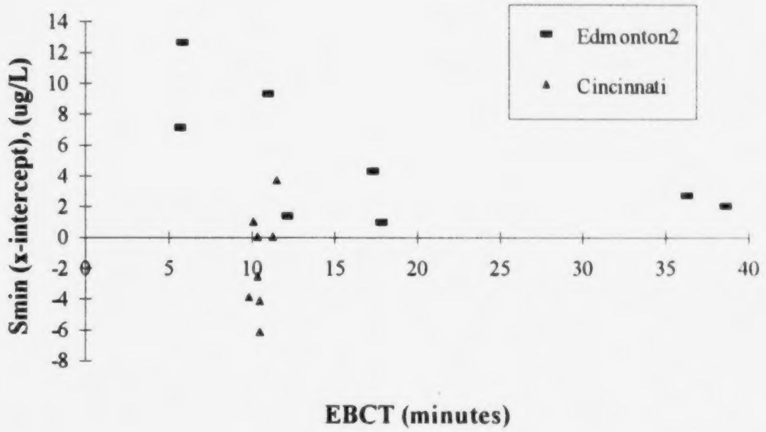


Figure 40: Minimum Achievable DCAAFP Concentration vs. EBCT

5.4.2 Trichloroacetic Acid Formation Potential (TCAAFP).

Edmonton, Alberta, 1992-1993

The Edmonton, Alberta study reported TCAAFP for influents and effluents of dual media filters and GAC contactors. The apparent first order rate constant and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercepts were calculated to determine the minimal achievable level. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 22 and a graphical presentation for each filter and GAC contactor is displayed in Appendix B, Figures B21 to B22.

Table 22

TCAAFP Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (μg/L)	y-intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	-0.033± 0.070	39	1.318 ± 4.860	0.39‡	5.3-5.5
Filter 2	0.145 ± 0.033	26	-3.709 ± 1.869	0.96	5.5-6.1
Filter 3	0.060 ± 0.041	14	-0.862± 2.255	0.90†	10.8-11.3
Filter 4	0.052 ± 0.011	4.3	-0.224 ± 0.619	0.97	8.8-15.7
Filter 5	0.097± 0.031	15	-1.421 ± 4.087	0.95	5.9-5.5
GAC 2	0.042± 0.013	2.3	-0.098 ± 0.388	0.93	17.2-18.4
GAC 3	0.025 ± 0.011	1.7	-0.043 ± 0.063	1.00	34.5-38.1
GAC 4	0.024 ± 0.003	4.9	-0.117 ± 0.077	0.99	34.5-42.7
GAC 5	0.050 ± 0.008	2.2	-0.108 ± 0.727	0.97	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, filter 5 (non-ozonated stream) produced an apparent rate constant of 0.097 min^{-1} and a correlation coefficient of 0.95, which was significant at the 1% level. The chlorinated stream (Filter 1) was determined to have an apparent first order rate constant of 0.033 min^{-1} and a correlation coefficient of 0.39 which was not significant at the 5% level. The calculated apparent rate constants for the ozonated streams ranged from 0.052 to 0.15 min^{-1} and correlation coefficients ranged from 0.90 to 0.97. All were significant at the 1% level, except for the correlation coefficient for Filter 3, which was significant at the 5% level. The x-intercept ranged between 4.3 and 26 μg/L (excluding Filter 1) indicating a wide range for the minimum achievable concentration. The results for these filters showed a good linear pattern. The graphical relationship is shown in Figure 41 for Filter 2. The apparent rate constants appear to vary according to the hydraulic loading rate as seen with DCAAFP. In addition, it was observed that the ozonated stream 2 produced a higher apparent rate constant then the non-ozonated stream 5. However, further comparison of these streams revealed that the x-intercept for Filter 2 was higher than for Filter 5.

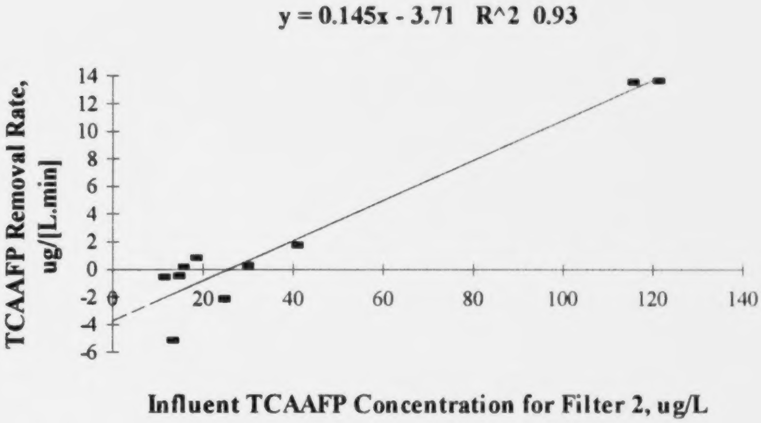


Figure 41: TCAAFP Removal Rate vs. Influent Concentration for Filter 2, Edmonton, 1992-93 Study

For the second stage filtration, the GAC contactors where hydraulically loaded at two rates, 4 and 8 m/h. The results gave apparent first order rate constants varying from 0.024 to 0.050 min^{-1}. The x-intercept ranged between 1.7 to 4.9 μg/L indicating a lower minimum achievable concentration than the first stage filtration. All the GAC contactors showed good linearity, and all correlation coefficients were significant at least at the 1% level. All GAC contactors obtained an x-intercept in the same range. The Pica GAC (stream 4) resulted in the highest x-intercept. The linear relationship for GAC 4 is displayed in Figure 42.

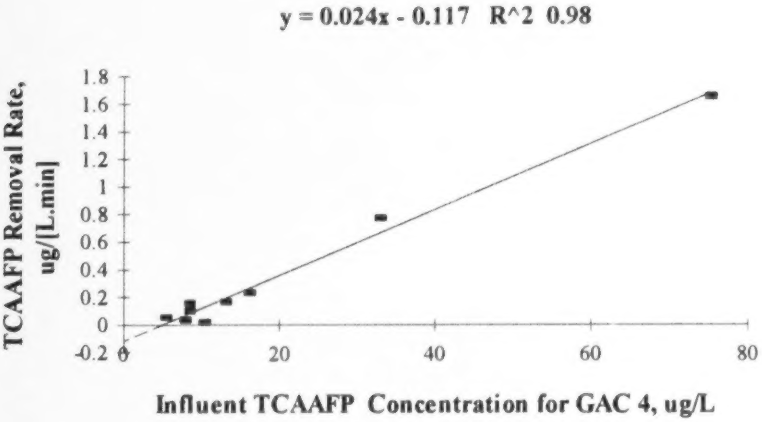


Figure 42: TCAAFP Removal Rate vs. Influent Concentration for GAC 4, Edmonton, 1992-93 Study

In general it would appear that during both first and second stage filtration, the apparent first order rate constant was dependent on hydraulic loading rate. Therefore, the higher EBCTs would typically show lower apparent rate constants. These results indicate that little removal was achieved in the lower portion of the bed for streams with low hydraulic loading. The y-intercepts for all the filters and GAC contactors were negative in all cases, (although most confidence intervals included zero), indicating that there was a minimum concentration below which the biodegradable material could not be reduced biologically.

Table 23 displays the results from a profile of TCAAFP concentrations at various positions of streams 2 and 4 during a spring run-off event. For stream 2, both the cumulative and segment apparent rate constants calculated for positions in the stream include negative values for the filter. In GAC 2, the apparent rate constants decreased with depth, as expected. For stream 4, the apparent rate constants in the both the filter and GAC show a decrease with depth for the cumulative rate constants and a positive value for the segment rate constants. In general, stream 2 (low EBCT) showed higher apparent rate constants than stream 4 (higher EBCT), within the segments of the columns. This is consistent with the above analysis for the entire depths. The segment apparent rate constants are graphically displayed in Figure 43. The filter adsorber (Filter 4) appeared to show higher apparent rate constants along segments than Filter 2.

Table 23
TCAAFP Profile Results for Streams 2 and 4

Location	TCAAFP (µg/L)	Segment Apparent Rate Constants (min^{-1})	Cumulative Apparent Rate Constant (min^{-1})
Following Ozonation	24.88		
Filter 2-31cm	28.47	-0.074	-0.074
Filter 2-61 cm	37.08	-0.128	-0.160
Filter 2-91 cm	37.25	-0.080	0.011
GAC 2-10 cm	29.82	0.237	0.237
GAC 2-47 cm	19.52	0.131	0.124
GAC 2-230 cm	5.85	0.049	0.051
Following Ozonation	51.83		
Filter 4-31cm	30.65	0.106	0.106
Filter 4-62 cm	30.09	0.055	0.005
Filter 4-91 cm	29.40	0.038	0.006
GAC 4-23 cm	19.51	0.095	0.095
GAC 4-47 cm	16.11	0.063	0.047
GAC 4-230 cm	8.98	0.020	0.016

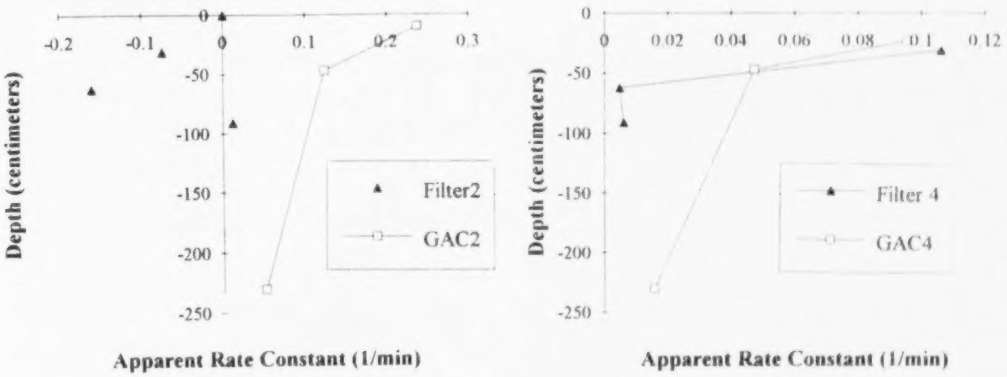


Figure 43: TCAAFP Apparent Rate Constant Profile for Streams 2 and 4, Edmonton, Alberta, 1992-1993 Study

Woodbridge, CT

The Woodbridge study reported TCAAFP, which was determined by a procedure using micro-extraction with methyl-t-butyl ether, and methylation (USEPA method 552; EMSL 1990; Hwany et al., 1990). This was the same method employed in the above Edmonton study. As noted in the DCAAFP section it was unfortunate that the hydraulic loading rate was doubled for two sampling days during the study. The apparent rate constants were calculated with their 95% confidence intervals for each stream. The correlation coefficients were determined and were not significant at the 5% level. It was decided at this stage to attempt to analyze the data using the lower hydraulic loading rate (also completed for AOC data) despite the indication that this rate was changed during the study. After the re-analysis of the data using the same hydraulic loading rate a better relationship was apparent. The results for Filter 1, the ozonated GAC/sand filter is shown in Figure 44. The graphs for the remaining filters can be found in Appendix B, Figure B23. The apparent first order rate constants, y-intercept, x-intercept, and correlation coefficients for all filters are tabulated in Table 24. The results for Filters 1 through 5 gave apparent rate constants from 0.087 to 0.10 min $^{-1}$, and correlation coefficients ranged from 0.99 to 1.00 which were all significant at the 1% level. Although caution must be used in comparing these data with other studies, since the true EBCT was not used consistently in the analysis, they are useful to confirm that the TCAAFP data is dependent on hydraulic rate.

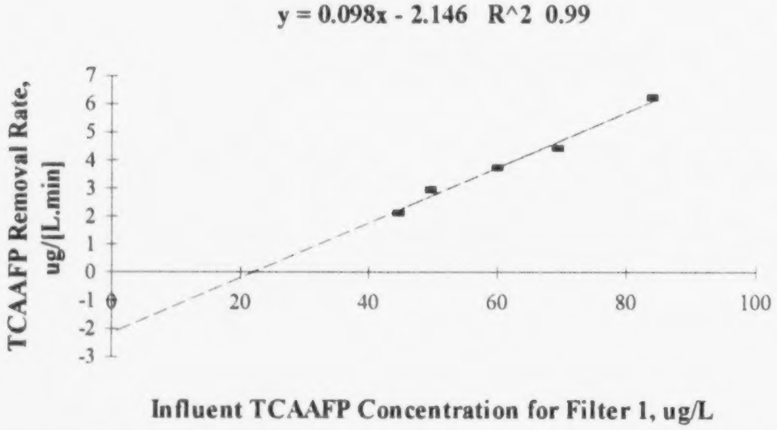


Figure 44: TCAAFP Removal Rate vs. Influent Concentration for Filter 1, Woodbridge, CT Study

Table 24

TCAAFP Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.098 ± 0.022	22	-2.146± 1.397	0.99	6.2-12.2
Filter 2	0.091 ± 0.030	20	-1.793± 1.791	0.99	6.2-12.2
Filter 3	0.087 ± 0.017	25	-2.155 ± 2.81	1.00	6.2-12.2
Filter 4	0.100± 0.017	15	-1.530 ± 1.271	1.00	6.2-12.2
Filter 5	0.095 ± 0.011	37	-3.537 ± 0.921	1.00	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

Discussion and Comparison of TCAAFP

In an attempt to discuss and compare the TCAAFP results for all the studies, two graphs were generated. Figure 45 displays the calculated apparent rate constants versus the EBCT and Figure 46 indicates the minimum achievable TCAAFP concentration versus EBCT. These figures were generated only using apparent rate constants for streams showing significant linearity. In general it appeared that chlorinated and chlorinated backwashed streams exhibited poor linearity and lower apparent rate constants than ozonated streams. Both first stage filtration and second stage filtration indicated excellent linearity. As with AOC and DCAAFP data it was observed that the apparent rate constants were dependent on EBCT. This relationship is shown in Figure 45, using only the data from Edmonton and Woodbridge. The Edmonton study clearly indicates a non-linear relationship between the apparent rate constant and EBCT. The Woodbridge study is difficult to compare with the Edmonton study since an average between the two EBCTs was used to generate this graph. If a lower EBCT was used to graph the Woodbridge results is would correspond to the steepest portion of the Edmonton curve.

To better define the non-linear relationship, several equation forms were employed to fit the curve. An equation in the form $x = ae^{-by}$ was found to best define the relationship. The equations were developed through a trial and error process, and a Least Squares analysis was not performed. This curve fit only intended to provide a semi-quantitative basis for comparision. The equation for TCAAFP apparent rate constants and EBCT is:

$$\text{EBCT} = 0.25 \times e^{-(0.080 \times \text{TCAAFP apparent rate constant})}$$

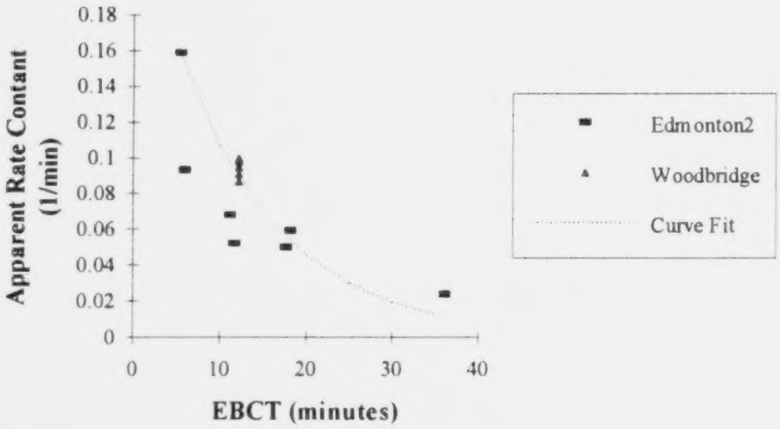


Figure 45: TCAAFP Apparent Rate Constant vs. EBCT

It was noted that for the Woodbridge study, the apparent rate constants may be inflated, since some removal may have occurred during coagulation. There was no way of knowing how much was removed during coagulation but this should be noted when interpreting the results.

The x-intercepts versus EBCT plot (Figure 46) would indicate a possible relationship for the Edmonton data. As mentioned with the DCAAFP results, the x-intercept does appear to decrease at the second stage filtration. The Woodbridge study typically indicates higher x-intercepts than the Edmonton Study. The range of influent TCAAFP for the Woodbridge study was 44.7 to 125 µg/L. The range of influent for the Edmonton study was 11.2 to 139 µg/L. Perhaps since the Woodbridge study did not experience TCAAFP concentrations as low as the Edmonton study the x-intercept was determined to be higher than in the Edmonton study.

Figure 46 suggest an EBCT at which there is no further decrease in S_{min} (x-intercept). The Edmonton data suggest that anything more than 15 minutes will not produce lower TCAAFP concentrations. The minimum x-intercept value achieved at 15 minutes is approximately 5 µg/L.

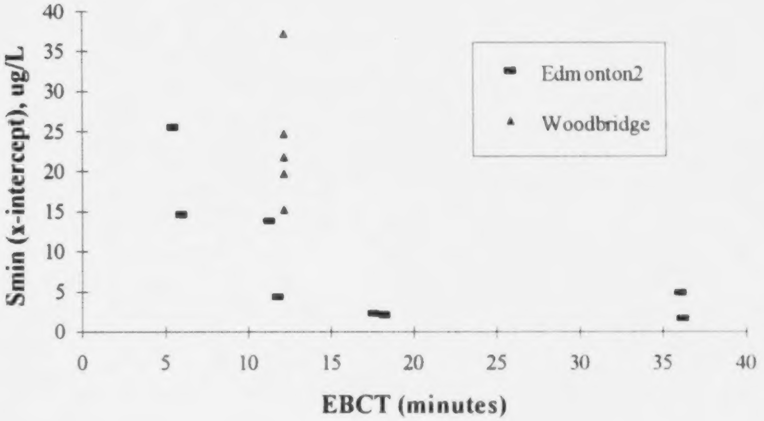


Figure 46: Minimum Achievable TCAAFP Concentration vs. EBCT

5.5. Chloral Hydrate Formation Potential

Edmonton, Alberta, 1992-1993 Study

The Edmonton, Alberta study reported chloral hydrate formation potential (CHFP) for influents and effluents of dual media filters and GAC contactors. The apparent first order rate constants and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercepts were calculated to determine the minimal achievable concentration. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 25 and a graphical presentation for each filter and GAC contactor is displayed in Appendix B, Figures B24 and B25.

Table 25
CHFP Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (μg/L)	y-intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	-0.017± 0.026	19	0.314 ± 0.548	0.53‡	5.3-5.5
Filter 2	0.025 ± 0.030	-1.8	0.044 ± 0.829	0.70‡	5.5-6.1
Filter 3	0.016 ± 0.041	-4.1	0.066± 0.830	0.47‡	10.8-11.3
Filter 4	0.046 ± 0.009	-3.4	0.155 ± 0.264	0.98	8.8-15.7
Filter 5	0.031± 0.042	3.7	-0.115 ± 0.626	0.51‡	5.9-5.5
GAC 2	0.054± 0.011	2.4	-0.130 ± 0.287	0.98	17.2-18.4
GAC 3	0.028 ± 0.006	2.1	-0.060 ± 0.095	0.99	34.5-38.1
GAC 4	0.024 ± 0.014	3.8	-0.092 ± 0.137	0.87	34.5-42.7
GAC 5	0.048 ± 0.012	2.7	-0.131 ± 0.163	0.95	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, Filter 5 (non-ozonated stream), produced an apparent rate constant of 0.031 min^{-1} and a correlation coefficient of 0.51, which was not significant at the 5% level. The chlorinated stream (Filter 1) was determined to have an apparent first order rate constant of -0.017 min^{-1} and a correlation coefficient of 0.53 which was not significant at the 5% level. The calculated apparent rate constants for ozonated streams (2 and 3) were 0.016 to 0.025 min^{-1} respectively and correlation coefficients were not significant at the 5% level. The filter absorber (stream 4) produced the only correlation coefficient significant at the 1% level, being 0.98. The apparent rate constant was determined to be 0.046 min^{-1} . The x-intercept ranged between -4.1 and 3.7 μg/L (excluding Filter 1) indicating a low but variable value range of the minimal achievable concentration. The results for these filters showed a good linear pattern. The graphical relationship is shown in Figure 47 for Filter 4. The apparent rate constants appear to vary according to the hydraulic loading rate as seen with DCAAFP (and other parameters).

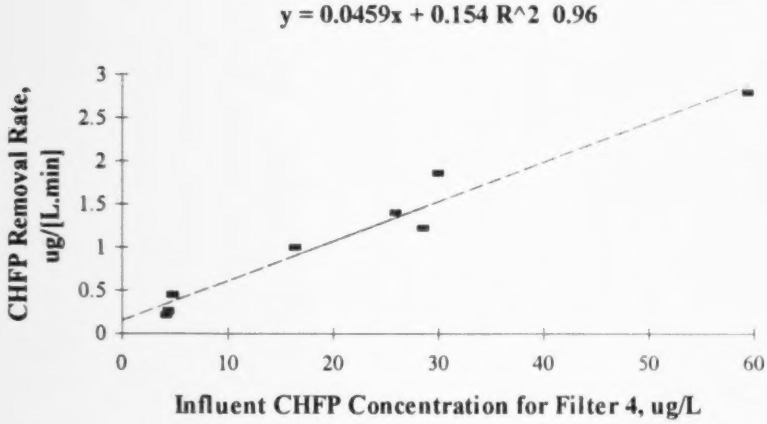


Figure 47: Chloral Hydrate Formation Potential Removal Rate vs. Influent Concentration for Filter 4, Edmonton, 1992-93 Study

For the second stage filtration, the GAC contactors were hydraulically loaded at two rates, 4 and 8 m/h. The results gave apparent first order rate constants varying from 0.024 to 0.054 min^{-1}. The x-intercept ranged between 2.1 and 3.8 μg/L indicating a similar minimum achievable concentration as the first stage filtration. All the GAC contactors showed good linearity, and all correlation coefficients were significant at least at the 1% level. All GAC contactors obtained an x-intercept in the same range. The Pica GAC (stream 4) resulted in the highest x-intercept. The linear relationship for GAC 4 is displayed in Figure 48.

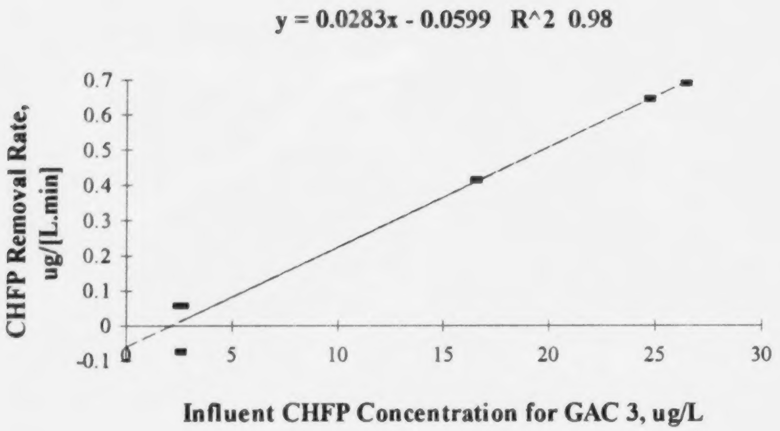


Figure 48: Chloral Hydrate Formation Potential Removal Rate vs. Influent Concentration for GAC 3, Edmonton, 1992-93 Study

In general it would appear that during both first and second stage filtration, the apparent first order rate constant was dependent on hydraulic loading rate. Therefore, the higher EBCTs would typically show lower apparent rate constants. These results indicate that little removal was achieved in the lower portion of the bed for the low hydraulic loading streams. The y- intercepts for all the filters and GAC contactors were negative, indicating that there was a minimum concentration below which the biodegradable material could not be reduced biologically. It was noted that only the columns containing GAC produced statistically significant correlations, indicating that adsorption may have contributed to the apparent first order relationship. However the number of data points available was quite small; additional data may have produced a better fit in the non-GAC filters.

5.6 Adsorbable Organic Halide Formation Potential (AOXFP)

Edmonton, Alberta, 1989-1990

The Edmonton, Alberta, 1989-90 study reported AOXFP for the influent and effluents for four dual media filters and three GAC contactors. These data was analyzed using individual data points (Appendix B, Figure B26 and B27) and apparent first-order rate constants were calculated with their 95% confidence intervals (Table 26). The x-intercepts were determined to obtain the minimum achievable concentration. The correlation coefficients were also calculated and their significant level determined.

Table 26
AOXFP Summary for Edmonton, 1989-90 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (µg/L)	y-intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.033 ± 0.008	49	-1.479± 2.964	0.93	9
Filter 2	0.068 ± 0.031	119	-8.072 ± 11.08	0.81	4.5
Filter 3	0.018 ± 0.013	-102	1.832 ± 4.204	0.65†	9
Filter 4	0.019 ± 0.051	-380	7.211 ± 16.79	0.26‡	4.5
GAC 2	0.031 ± 0.008	41	-1.280 ± 2.376	0.92	19
GAC 3	0.024 ± 0.004	29	-0.697± 1.144	0.96	36
GAC 4	0.032 ± 0.010	34	-1.086 ± 2.780	0.90	19

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, the calculated apparent first-order rate constants varied from 0.018 to 0.068 min^{-1} filters. The x-intercepts values ranged between -102 and 119 µg/L for filters with statistically significant correlations. The correlation coefficients varied between 0.26 and 0.93 and all correlation coefficients were significant at least at the 5% level except for Filter 4. The first order rate constants appeared to vary according to the EBCT, with the exception to Filter 4 (due to its poor linearity). All Filters except Filter 4 showed at least reasonable linearity and this relationship is shown in Figure 49 for Filter 1. In general, the higher the EBCT, the lower the apparent first-order rate constant. This observation would indicate that the same degree of AOXFP removal was achieved for both hydraulic loading rates, and at the low hydraulic loading rate, little removal was achieved in the lower portion of the bed.

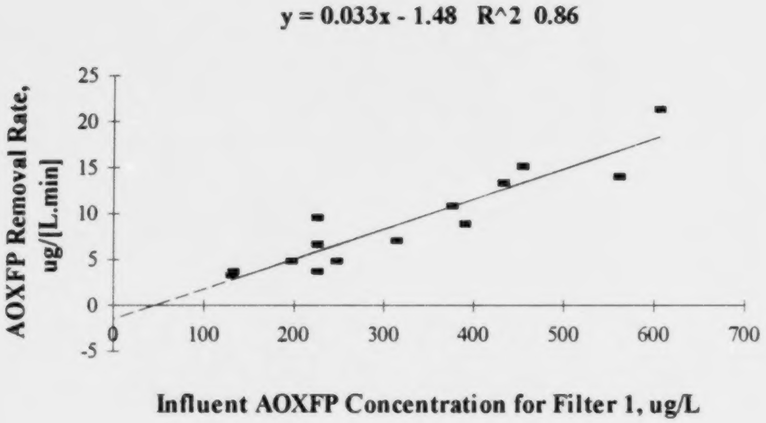


Figure 49 AOXFP Removal Rate vs. Influent Concentration for Filter 1, Edmonton, 1989-90

For the second stage filtration, the results gave apparent first order rate constants varying from 0.024 to 0.032 min^{-1}. The x-intercept ranged from 29 to 41 µg/L, a significantly lower x value than in the first stage filtration. The correlation coefficients indicated good linearity, varying from 0.90 to 0.96. All the correlation coefficients were significant at least at the 1% level. The graphical relationship for GAC 3 is shown in Figure 50. As with the dual media filtration, the apparent first-order rate constants appear to be dependent on hydraulic loading rate, where higher EBCTs yielded lower apparent rate constants.

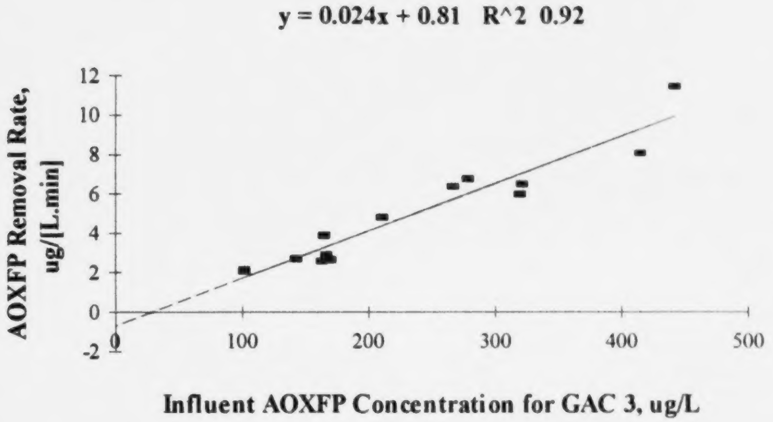


Figure 50 AOXFP Removal Rate vs. Influent Concentration for GAC 3, Edmonton, 1989-90

In general, there appeared to be some scatter in the data for the dual media filtration, and better linearity in the GAC contactors. Except in one case, the x-intercepts for all filters and GAC contactors were positive whenever the correlations coefficients were significant, indicating that there was a minimum concentration below which the biodegradable material could not be reduced biologically (All negative y-intercepts included zero in the 95% confidence interval however). It was observed that the higher x-intercepts were attributed to the higher hydraulic loading rate.

Edmonton, Alberta 1992-1993

The Edmonton, Alberta 1992-1993 study also reported AOXFP for influents and effluents for dual media filters and GAC contactors. The apparent first order rate constants, and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercept was determined to obtain the achievable removal concentration. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 27 and a graphical presentation for each filter and GAC contactors is displayed in Appendix B, Figures B28 and B29. It should be noted that considerably fewer data points were available for this than for the previous Edmonton study.

Table 27

AOXFP Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.085 ± 0.064	154	-13.08 ± 14.44	0.80†	5.3-5.5
Filter 2	0.094 ± 0.097	172	-16.17 ± 20.86	0.75‡	5.5-6.1
Filter 3	0.050 ± 0.042	142	-7.078± 9.257	0.86†	10.8-11.3
Filter 4	0.095± 0.105	110	-10.47 ± 22.97	0.67‡	8.9-15.7
Filter 5	0.020 ± 0.053	-81	1.623 ± 16.24	0.27‡	5.9-5.5
GAC 2	0.049 ± 0.011	22	-1.058± 2.792	0.97	17.2-18.4
GAC 3	0.021 ± 0.005	-27	0.566± 1.179	0.97	34.5-38.8
GAC 4	0.011 ± 0.008	-18	0.195 ± 0.772	0.83†	34.5-42.7
GAC 5	0.019 ± 0.011	-302	5.733 ± 2.837	0.85	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, Filter 1 yielded an apparent rate constant of 0.085 min^{-1} , and a correlation coefficient which was significant at the 5% level. The non-ozonated stream (Filter 5) was analyzed and an apparent rate constant of 0.020 min^{-1}, was determined but the correlation coefficient was not significant at the 5% level. For the ozonated streams (Filters 2, 3 and 4), apparent rate constants ranged from 0.050 to 0.095 min^{-1}, and correlation coefficients ranged for 0.67 to 0.86. The coefficients were not significant at the 5% level for Filters 2, 3 and 4, and a large amount of scatter was noted in these filters. The graphical relationship for Filter 2 is shown in Figure 51.

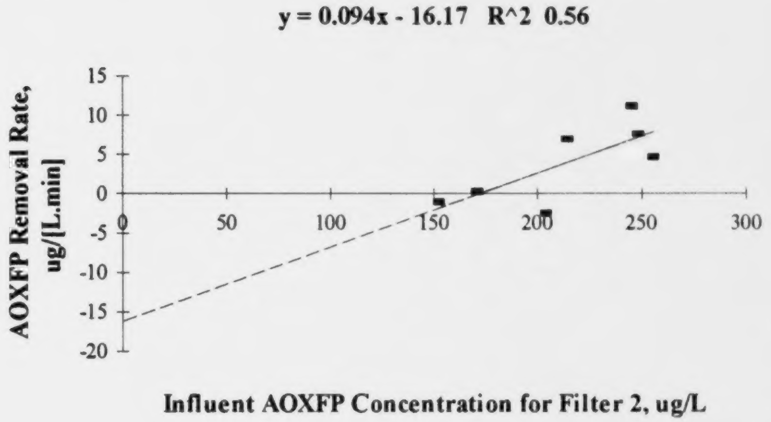


Figure 51 AOXFP Removal Rate vs. Influent Concentration for Filter 2 Edmonton, 1992-93

For the second stage filtration, results gave apparent first order rate constants varying from 0.011 to 0.049 min^{-1}. All the GAC contactors show good linearity, and all correlation coefficients were significant at least at the 5% level. The graphical relationship for GAC 3 is shown in Figure 52. The Pica carbon (GAC 4) had the lowest apparent rate constant and the ozonated stream with the highest hydraulic loading (GAC 2) had the highest apparent rate constant. These results correspond to the same trend noticed in the NVOC analysis. It would also appear that the apparent rate constants are dependent on hydraulic loading rate, where higher EBCT contactors show little removal in the lower portion of the bed. The x-intercepts calculated were both negative and positive, with the lower apparent rate constants produce negative x-intercepts.

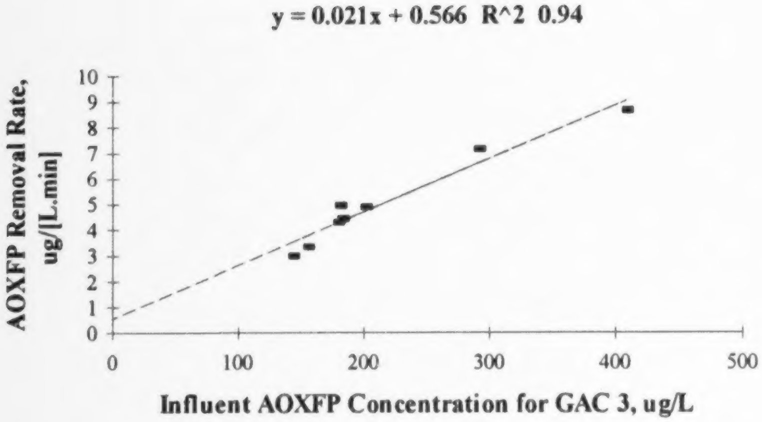


Figure 52 AOXFP Removal Rate vs. Influent Concentration for GAC 3 Edmonton, 1992-93

Discussion and Comparison for AOXFP

In an attempt to discuss and compare the AOXFP results from the two Edmonton studies, two graphs were generated. Figure 53 displays the calculated apparent rate constants versus the EBCT and Figure 54 indicates the minimum achievable AOXFP concentration versus EBCT. These figures were generated only using apparent rate constants for streams showing significant linearity. In general it appeared that the first stage filtration does indicate some significant linearity, however better linearity is observed at the second stage filtration. Due to the poor linearity observed in the filter adsorber for the most recent Edmonton study, it would appear that AOXFP removal was not influenced significantly by adsorption. It was noted that the apparent rate constants appeared to be dependent on EBCT. Figure 53, indicates that a possible non-linear relationship would exist between these parameters, as was seen in the AOC and HAAFP data.

To better define the non-linear relationship, several equation forms were employed to fit the curve. An equation in the form $x = ae^{-by}$ was found to best define the relationship. The equations were developed through a trial and error process, and a Least Squares analysis was not performed. This curve fit only intended to provide a semi-quantitative basis for comparision. The equation for AOXFP apparent rate constants and EBCT is:

$$\text{EBCT} = 0.10 \times e^{-(0.055 \times \text{AOXFP apparent rate constant})}$$

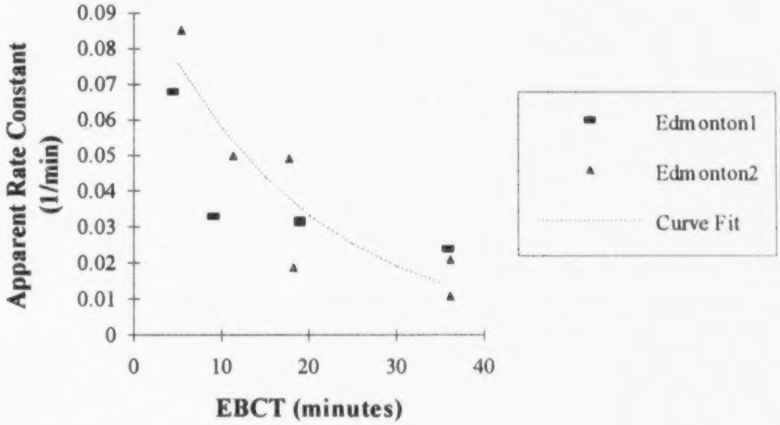


Figure 53: AOXFP Apparent Rate Constant vs. EBCT

The x-intercepts were plotted against the EBCT in Figure 54. It would appear that the x-intercepts decreased significantly in the second stage filtration, however these trends could only be expressed qualitatively. The range of AOXFP influent concentrations for the Edmonton 1989-90 study was from 14 to 607 μg/L. The range of influents for the Edmonton 1992-93 study was from 53 to 458 μg/L. These ranges were similar and the x-intercepts for these studies appear also to be in the same range. For EBCTs greater than approximately 20 minutes there is little if any further change in the x-intercept. The value than corresponds to the 20 minute EBCT is approximately 30 μg/L.

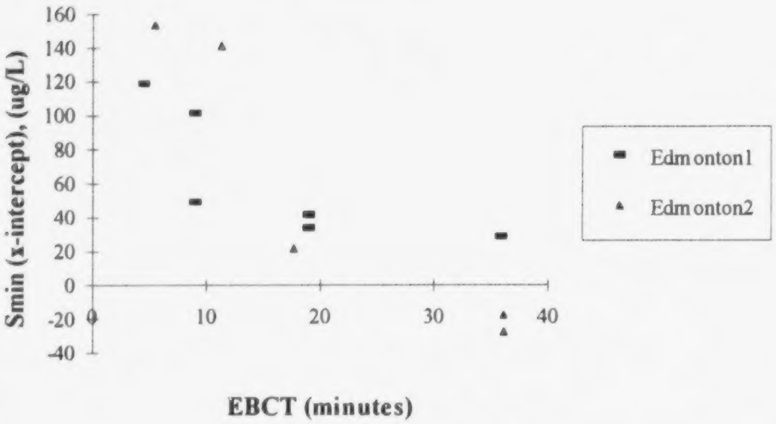


Figure 54: Minimum Achievable AOXFP Concentration vs. EBCT

5.7 Trihalomethane Formation Potential (THMFP)

Edmonton, Alberta 1989-1990 Study

The Edmonton, Alberta, 1989-90 study reported THMFP for the influents and effluents for four dual media filters and four GAC contactors. These data were analyzed using individual data points and apparent first-order rate constants were calculated with their 95% confidence intervals reported (Table 28). The x-intercepts were determined to obtain the minimum achievable concentration. The correlation coefficients were also calculated and the significant level determined. The results of this analysis are displayed graphically in Appendix B, Figures B30 and B31.

Table 28

THMFP Summary for Edmonton, 1989-90 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (µg/L)	y-intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.031 ± 0.010	12	-0.361± 1.387	0.78	9
Filter 2	0.075 ± 0.057	79	-5.892 ± 7.640	0.46†	4.5
Filter 3	0.028 ± 0.006	31	-0.862 ± 0.748	0.88	9
Filter 4	0.042 ± 0.023	72	-3.024 ± 2.810	0.60	4.5
GAC 1	0.026 ± 0.002	2.0	-0.052± 0.148	0.99	36
GAC 2	0.046 ± 0.007	14	-0.623 ± 0.430	0.94	19
GAC 3	0.025 ± 0.001	4.4	-0.110± 0.112	0.99	36
GAC 4	0.049 ± 0.003	5.7	-0.279 ± 0.285	0.99	19

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, the calculated apparent first-order rate constants varied from 0.028 to 0.075 min^{-1} for all four filters. The x-intercepts values ranged between 12 to 79 µg/L. The correlation coefficients varied between 0.46 and 0.88 and all correlation coefficients were significant at least at the 5% level. The first order rate constants appeared to vary according to the EBCT, and all filters showed some linearity. This relationship is shown in Figure 55 for Filter 3. In general, the higher EBCT, the lower the apparent first-order rate constant. This observation would indicate that the same degree of THMFP removal was achieved for both hydraulic loading rates, and at the low hydraulic loading rate, little removal was achieved in the lower portion of the bed.

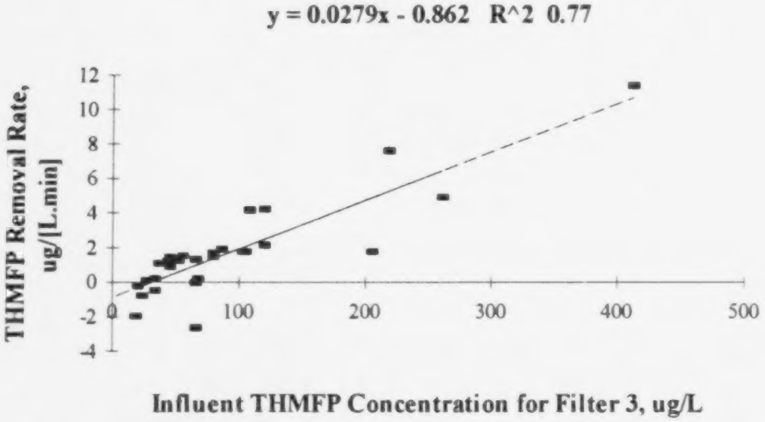


Figure 55 THMFP Removal Rate vs. Influent Concentration for Filter 3, Edmonton 1989-90

For the second stage filtration, the results gave apparent first order rate constants varying from 0.025 to 0.049 min^{-1}. The x-intercept ranged from 2.0 to 14 µg/L, indicating a significantly lower x-intercept value than in the first stage filtration. The correlation coefficients indicated good linearity, with coefficients varying from 0.94 to 0.99. The graphical relationship for GAC 4 is shown in Figure 56. All the correlation coefficients were significant at least at the 1% level. As with the dual media filtration, the apparent first-order rate constants appear to be dependent on hydraulic loading, where higher EBCTs yielded lower apparent rate constants.

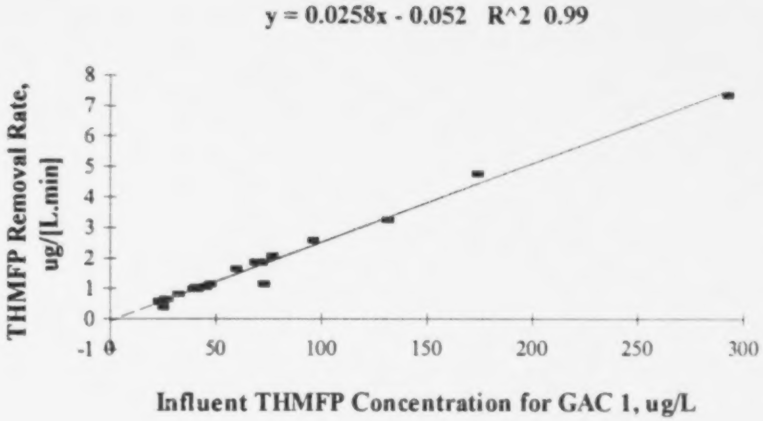


Figure 56 THMFP Removal Rate vs. Influent Concentration for GAC 1, Edmonton, 1989-90

In general, there appeared to be only slight scatter in the data for the dual media filtration, and better linearity in the GAC contactors. The x-intercepts for all filters and GAC contactors were positive, indicating that there was a minimum concentration below which the biodegradable material could not be reduced biologically. It was observed that the higher x-intercepts were attributed to the higher hydraulic loading streams.

Edmonton, Alberta 1992-1993

The Edmonton, Alberta study reported THMFP for influents and effluents for dual media filters and GAC contactors. The apparent first order rate constants, and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercept was determined to obtain the minimum concentration. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 29 and a graphical presentation for each filter and GAC contactor is displayed in Appendix B, Figures B32 and B33.

Table 29
THMFP Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.057 ± 0.040	28	-1.606 ± 2.367	0.82†	5.3-5.5
Filter 2	0.138 ± 0.060	24	-3.357± 3.130	0.89	5.5-6.1
Filter 3	0.059± 0.159	17	-0.997 ± 3.528	0.75‡	10.8-11.3
Filter 4	0.038± 0.021	-7.6	0.288 ± 0.994	0.85	8.8-15.7
Filter 5	0.129 ± 0.427	28	-3.640 ± 13.94	0.98‡	5.9-5.5
GAC 2	0.045 ± 0.014	-7.0	0.317± 0.450	0.99	17.2-18.4
GAC 3	0.025 ± 0.002	-1.7	0.040± 0.082	1.00	34.5-38.7
GAC 4	0.025 ± 0.004	4.6	-0.116± 0.103	0.99	34.5-42.7
GAC 5	0.035 ± 0.017	-6.8	0.239 ± 5.34	0.54‡	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, Filter 1 yielded an apparent rate constant of 0.057 min^{-1}, and a correlation coefficient which was significant at the 5% level. The non-ozonated stream (Filter 5) was analyzed and an apparent rate constant of 0.129 min^{-1} was calculated, but the correlation coefficient was determined not to be significant at the 5% level probably because of the small number of data points. For the ozonated streams (Filters 2, 3 and 4), apparent rate constants ranged from 0.038 to 0.138 min^{-1}, and correlation coefficients ranged from 0.75 to 0.89. The coefficients were significant at the 1% level for Filter 2 and 4, however fewer data points were available for Filter 3, and produced a correlation coefficient not significant at 5%. The graphical relationship for Filter 4 is shown in Figure 57. The x-intercepts ranged between -7.6 and 28 μg/L.

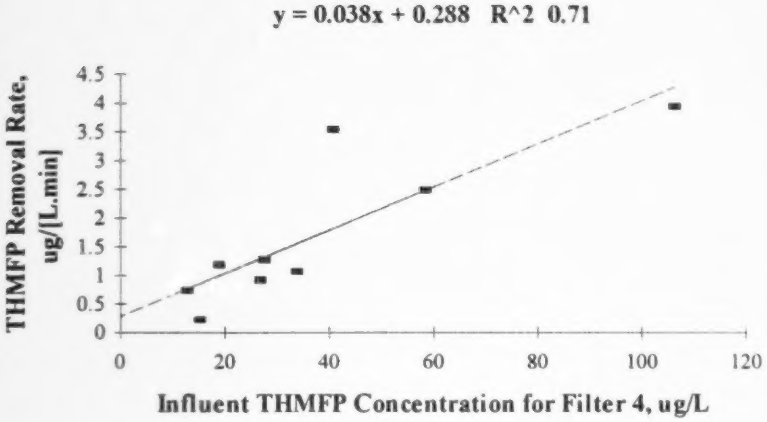


Figure 57 THMFP Removal Rate vs. Influent Concentration for Filter 4 Edmonton, 1992-93

For the second stage filtration, the results gave apparent first order rate constants varying from 0.025 to 0.045 min^{-1}. All the GAC contactors showed excellent linearity, and all correlation coefficients were significant at least at the 1% level. The graphical relationship for GAC 4 is shown in Figure 58. These results correspond to the same trend noticed in the NVOC analysis. It would also appear that the apparent rate constants are dependent on hydraulic loading rate, where higher EBCT contactors show little removal in the lower portion of the bed. The x-intercept ranged between -7.0 to 4.6 μg/L.

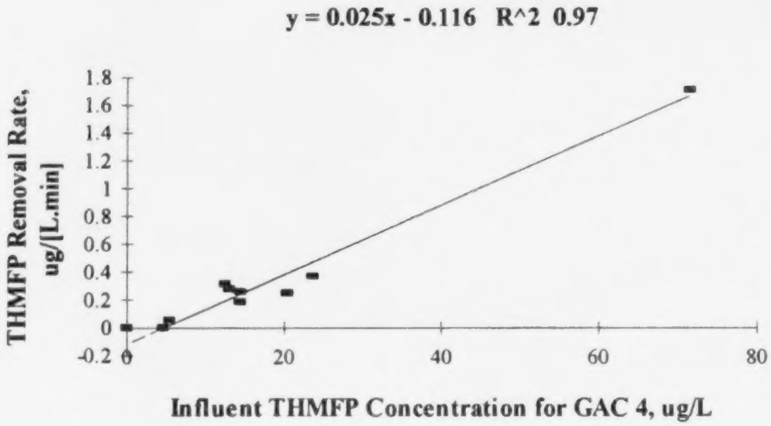


Figure 58 THMFP Removal Rate vs. Influent Concentration for GAC 4 Edmonton, 1992-93

Table 30 displays the results from a profile of THMFP concentrations at various positions of streams 2 and 4 during a spring run-off event. For stream 2, both the Filter 2 and GAC, it was found that the cumulative apparent rate constant decreased with depth. The segment apparent rate constant indicated an initial removal, then negative apparent rate constants throughout the filter. The segment apparent rate constant decreased with depth in GAC 2. In Stream 4, both the cumulative and segment apparent rate constants indicated a decrease followed by an increase with depth for Filter 4. For GAC 4, negative apparent rate constants were found. Filter 4 contains GAC, and had removed significantly more THMFP than Filter 2. Overall, stream 4 indicated a higher THMFP removal than stream 2. The segment apparent rate constants are displayed in Figure 59.

Table 30
Profile THMFP Results for Streams 2 and 4

Location	THMFP (µg/L)	Segment Apparent Rate Constant (min^{-1})	Cumulative Apparent Rate Constant (min^{-1})
Following Ozonation	30.38		
Filter 2-31 cm	22.49	0.133	0.133
Filter 2-61 cm	28.79	0.014	-0.149
Filter 2-91 cm	30.22	0.001	-0.026
GAC 2-10 cm	19.94	0.455	0.455
GAC 2-47 cm	15.93	0.072	0.072
GAC 2-230 cm	5.56	0.047	0.048
Following Ozonation	40.95		
Filter 4-31 cm	24.49	0.104	0.104
Filter 4-62 cm	20.73	0.065	0.040
Filter 4-91 cm	0.86	0.087	0.249
GAC 4-23 cm	13.92	-4.303	-4.303
GAC 4-47 cm	3.80	-0.474	0.197
GAC 4-230 cm	2.75	-0.062	0.010

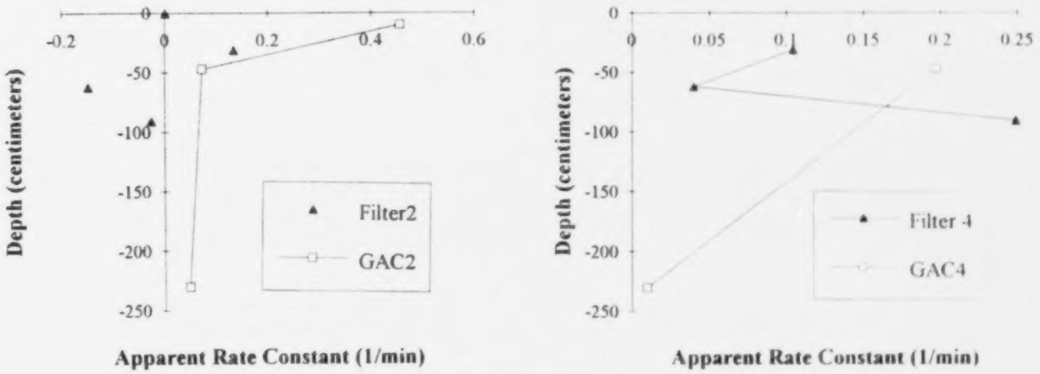


Figure 59: THMFP Apparent Rate Constants for Stream 2 and 4, Edmonton, Alberta, 1992-1993 Study

Laval, Quebec

The Laval, Quebec study measured THMFP, according to the procedure described in Standard Methods (APHA-AWWA-WPCP). Adequate data were not available for the dual media filtration, however data for the two BAC contactors were available in addition to profile data. Figure 60 displays the graphical analysis for BAC 2G contactor. Table 31 summarizes the apparent rate constants and y-intercepts with their 95% confidence intervals. The x-intercepts were determined to obtain a minimum achievable concentration. The correlation coefficient were calculated and their level of significance determined.

Table 31
THMFP Summary for Laval, Quebec Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
BAC 2G 10 cm	0.030 ± 0.065	-27	0.803 ± 9.615	0.46‡	5.0-7.0
BAC 2G 70 cm	0.011 ± 0.024	-40	0.441 ± 3.592	0.44‡	13.0-16.0
BAC 2G 130 cm	0.007 ± 0.016	-38	0.269 ± 2.283	0.45‡	20.0-26.0
BAC 2G Effluent	0.005 ± 0.011	-38	0.189 ± 1.66	0.45‡	28.0-36.0
BAC 5D 15 cm	0.075 ± 0.087	45	-3.400 ± 11.76	0.77‡	5.0-6.0
BAC 5D 80 cm	0.022 ± 0.027	27	-0.587 ± 3.670	0.75‡	13.0-16.0
BAC 5D 140 cm	0.014± 0.018	28	-0.390± 2.476	0.74‡	20.0-26.0
BAC 5D Effluent	0.010 ± 0.013	28	-0.275 ± 1.775	0.74‡	28.0-36.0

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5%

The second stage filtration employed a prior ozonation step and a design hydraulic loading rate of 4 m/h. Individual EBCTs for each sampling day were obtained and used in the calculation. The results for the two BAC contactors analyzed gave apparent first order rate constant of 0.005 and 0.010 min^{-1}, however neither correlation coefficient was significant at the 5% level. Apparent rate constants were determined for three locations along the depth of these contactors. The linear relationship had correlation coefficients not significant at the 5% level. Although these results were not significant, similar trends were observed in other Laval parameters. These results indicate a greater removal rate near the top of the contactors with decreasing removal rates with depth in the contactor as would be expected. The segment apparent rate constants were determined along the depth of the contactors, however every rate constant calculated indicated extremely poor linearity and none of the correlations were significant at the 5% level.

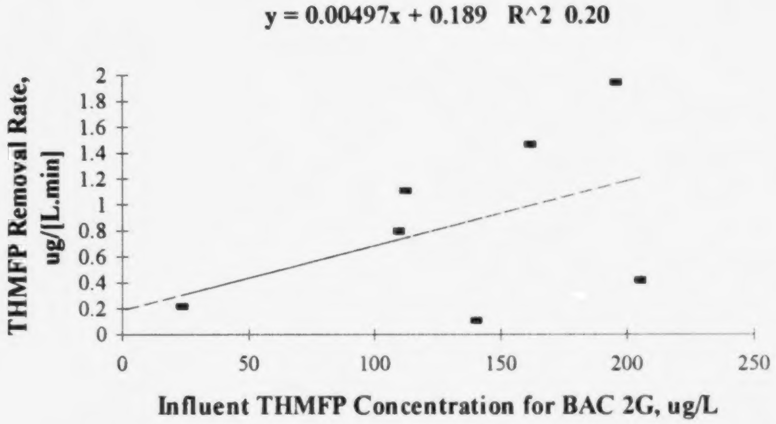


Figure 60: THMFP Removal Rate vs. Influent Concentration for BAC 2G, Laval, Quebec Study

Discussion and Comparison for THMFP

In an attempt to discuss and compare the THMFP results for the above studies, two graphs were generated. Figure 61 displays the calculated apparent rate constants versus EBCT and Figure 62 indicate the minimum achievable THMFP concentration versus EBCT. These figures were generated only using apparent rate constants for streams showing significant linearity, and therefore only included data from Edmonton. In general it appeared that the first stage filtration does indicate some significant linearity, however better linearity is observed at the second stage filtration. It was noted that the apparent rate constants appeared to decrease with EBCT (Figure 61). This relationship indicated a steeper slope for shorter EBCTs. After 5 minutes the slope tends to flatten, but continues to decrease up to 35 minutes.

To better define the non-linear relationship, several equation forms were employed to fit the curve. An equation in the form $x = ae^{-by}$ was found to best define the relationship. The equations were developed through a trial and error process, and a Least Squares analysis was not performed. This curve fit only intended to provide a semi-quantitative basis for comparision. The equation for THMFP apparent rate constants and EBCT is:

$$\text{EBCT} = 0.11 \times e^{-(0.045 \times \text{THMFP apparent rate constant})}$$

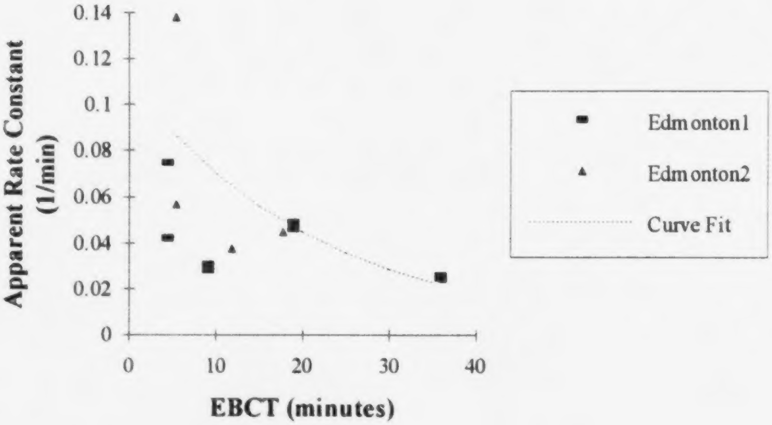


Figure 61: THMFP Apparent Rate Constant vs. EBCT

The x-intercept also decreases with EBCT (Figure 62). The trend shows lower x-intercepts as a result of a second filtration step. The Laval data were not included, since they were not linearly significant. The influent THMFP concentration for the Edmonton, 1989-90 study ranged from 16 to 413 µg/L, whereas the influent THMFP for the Edmonton, 1992-1993 study ranged from 12 to 136 µg/L. The Laval study influent ranged from 23 to 205 µg/L. It is interesting to note that the Edmonton studies produced similar x-intercepts, although the influent range for the 1989-90 study was significantly higher. There is only a small change in the x-intercept for EBCTs greater than approximately 20 minutes. Since the temperature in Laval exhibited greater fluctuations, this could have contributed to the poor linearity in the data.

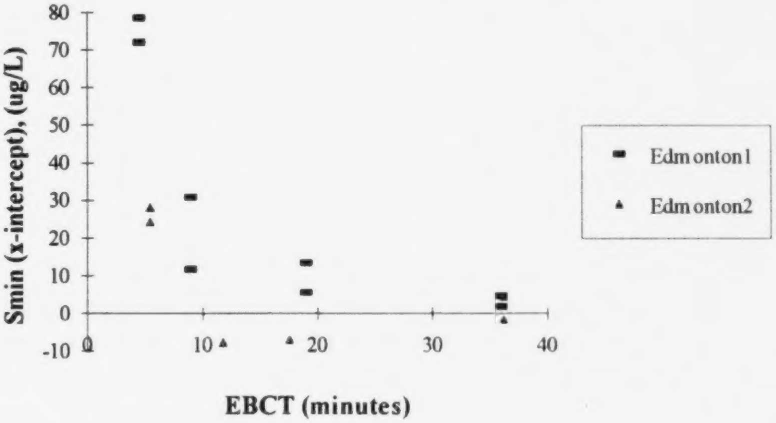


Figure 62: Minimum Achievable THMFP Concentration vs. EBCT

5.8 Chlorine Demand (CD)

Edmonton, Alberta 1989-1990 Study

The Edmonton, Alberta, 1989-90 study reported chlorine demand for the influents and effluents for four dual media filters and four GAC contactors. These data were analyzed using individual data points and apparent first-order rate constants were calculated with their 95% confidence intervals (Table 32). The x-intercepts were determined to obtain the minimum achievable concentration. The correlation coefficients were also calculated and the significance level determined. The results of this analysis are displayed graphically in Appendix B, Figures B35 and B36.

Table 32
Chlorine Demand Summary for Edmonton, 1989-90 Study

Stream	Apparent Rate* Constant (min^{-1})	x-intercept (mg/L)	y-intercept* (mg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.049 ± 0.021	3.2	-0.156± 0.167	0.92	9
Filter 2	0.092 ± 0.053	3.4	-0.313 ± 0.431	0.86	4.5
Filter 3	0.016 ± 0.029	-9.6	0.154 ± 0.304	0.45‡	9
Filter 4	0.038 ± 0.109	-2.3	0.088 ± 0.970	0.33‡	4.5
GAC 1	0.022 ± 0.009	0.4	-0.008± 0.050	0.99	36
GAC 2	0.029 ± 0.007	1.4	-0.040 ± 0.075	0.94	19
GAC 3	0.021 ± 0.003	1.5	-0.031± 0.0223	0.99	36
GAC 4	0.034 ± 0.007	2.1	-0.070 ± 0.074	0.97	19

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, calculated apparent first-order rate constants varied from 0.016 to 0.092 min^{-1} for all four filters. The x-intercept values ranged between -9.6 to 3.4 mg/L. The correlation coefficients varied between 0.33 and 0.86. Correlation coefficients for Filter 1 and 2 were significant at least at the 1% level, whereas those for Filter 3 and 4 were not significant at the 5% level. The graphical relationship for Filter 2 is shown in Figure 63.

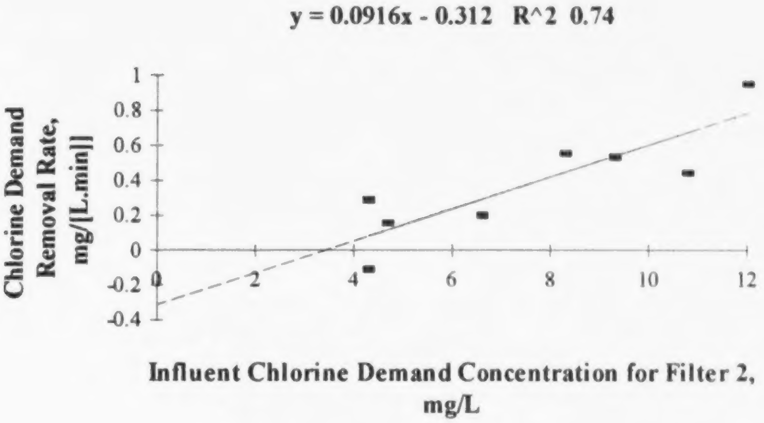


Figure 63 Chlorine Demand Removal Rate vs. Influent Concentration for Filter 2 Edmonton, 1989-90

For the second stage filtration, results gave apparent first order rate constants varying from 0.021 to 0.034 min^{-1}. The x-intercept ranged from 0.4 to 2.1, indicating a significantly lower x-intercept value than in the first stage filtration. The correlation coefficients indicated good linearity, varying from 0.94 to 0.99, and were all significant at least at the 1% level. The graphical relationship for GAC 4 is shown in Figure 64. As with the dual media filtration, the apparent first-order rate constants appear to be dependent on hydraulic loading rate, where higher EBCTs yielded lower apparent rate constants. Therefore, there was little advantage to the longer EBCTs.

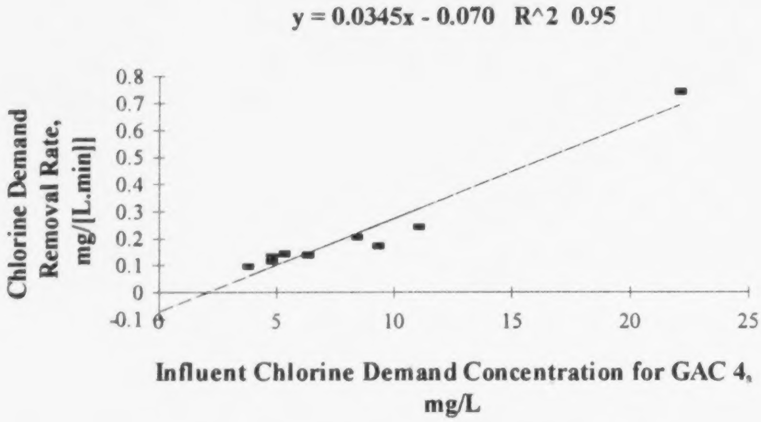


Figure 64 Chlorine Demand Removal Rate vs. Influent Concentration for GAC 4, Edmonton, 1989-90

In general, there appeared to be only moderate scatter in the data for the dual media filtration, and better linearity in the GAC contactors. The x-intercepts for the filters and GAC contactors were positive in all cases when the correlation was significant, indicating that there was a minimum concentration below which the biodegradable material could not be reduced biologically. It was observed that the higher x-intercepts were attributed to the higher hydraulic loading streams, although differences were not large.

Edmonton, Alberta 1992-1993

The Edmonton, Alberta study also reported chlorine demand for influents and effluents of the dual media filters and GAC contactors. The apparent first order rate constant and y-intercepts were calculated in addition to their 95 % confidence intervals. The x-intercepts was determined to obtain the minimum achievable concentration. The correlation coefficients and their significance level were determined for all streams. These results are tabulated in Table 33 and a graphical presentation for each filter and GAC contactor are displayed in Appendix B, Figure B37 and B38. For the filters, there was considerably more scatter in the data than for the 1989-1990 study.

Table 33

Chlorine Demand Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (mg/L)	y-Intercept* (mg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.012 ± 0.050	-3.4	0.041 ± 0.089	0.22‡	5.3-5.5
Filter 2	0.046 ± 0.027	10	-0.472± 0.088	0.45‡	5.5-6.1
Filter 3	0.075± 0.213	0.9	-0.067 ± 0.223	0.38‡	10.8-11.3
Filter 4	0.017± 0.092	-0.8	0.013 ± 0.097	0.15‡	8.8-15.7
Filter 5	0.054 ± 0.105	0.02	-0.001 ± 0.163	0.42‡	5.9-5.5
GAC 2	0.048 ± 0.008	0.3	-0.014± 0.011	0.97	17.2-18.4
GAC 3	0.030 ± 0.010	0.4	-0.013± 0.011	0.96	34.5-38.8
GAC 4	0.025 ± 0.003	0.4	-0.010± 0.003	0.99	34.5-42.7
GAC 5	0.061 ± 0.011	0.6	-0.035 ± 0.015	0.97	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, Filter 1 was a chlorinated stream and yielded an apparent rate constant of 0.012 min^{-1}, and a low correlation coefficient which was not significant at the 5% level. The non-ozonated stream (Filter 5) was analyzed and an apparent rate constant of 0.054 min^{-1} was calculated, but the correlation coefficient was determined not to be significant at the 5% level. For the ozonated streams (Filters 2, 3 and 4), apparent rate constants ranged from 0.017 to 0.075 min^{-1} and correlation coefficients ranged from 0.15 to 0.45. The coefficients were not significant at the 5% level for any of the ozonated filters. The graphical relationship for Filter 2 is shown in Figure 65.

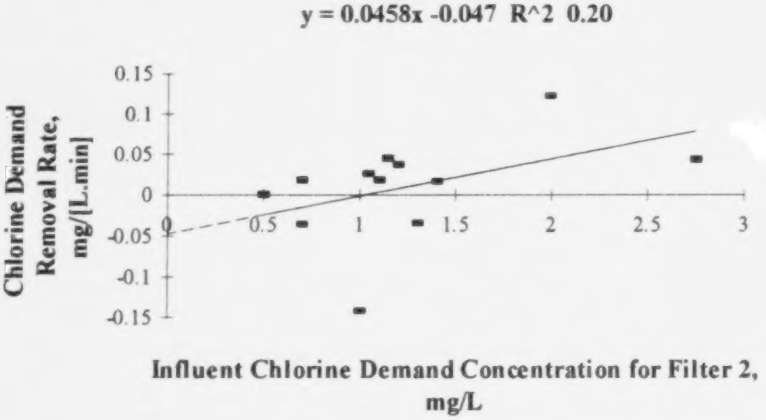


Figure 65 Chlorine Demand Removal Rate vs. Influent Concentration for Filter 2 Edmonton, 1992-93

For the second stage filtration, the results gave apparent first order rate constants varying from 0.025 to 0.061 min^{-1}. All the GAC contactors showed good linearity, and all correlation coefficients were significant at least at the 1% level. The graphical relationship for GAC 5 is shown in Figure 66. The Pica carbon (GAC 4) had the lowest apparent rate constant and the non-ozonated stream (GAC 5) had the highest apparent rate constant. The x-intercept ranged between 0.29 and 0.57 mg/L. These values were positive indicating there would a minimum concentration below which the biodegradable material could not be reduced biologically.

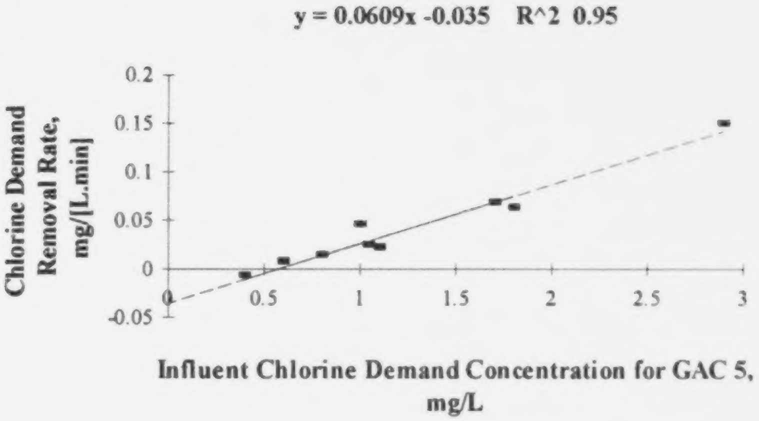


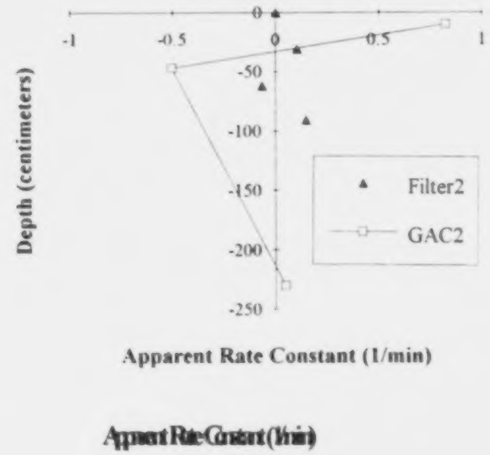
Figure 66 Chlorine Demand Removal Rate vs. Influent Concentration for GAC 5 Edmonton, 1992-93

Table 34 displays the results from a profile of chlorine demand concentrations at various positions of streams 2 and 4 during a spring run-off event. For stream 2, both the Filter 2 and GAC 2 show that the cumulative apparent rate constants decrease with depth. The segment apparent rate constant indicated an initial removal then negative apparent rate constants followed by positive apparent rate constants in Filter 2 and GAC 2. For Stream 4, the cumulative and segment apparent rate constants indicate both an increase and decrease with depth for Filter 4 and GAC 4. For the segment apparent rate constants, both negative and positive apparent rate constant were produced in this stream. In general the apparent rate constants both cumulatively and per segment appear to decrease with depth. The apparent rate constants for cumulative removal for first and second stage filtration were generally higher for Stream 2 (low EBCT) than stream 4 (high EBCT). This trend corresponds to what was observed in the above analysis for the entire filters or contactors. The segment apparent rate constants are graphically displayed in Figure 67.

Table 34

Profile Chlorine Demand Results for Streams 2 and 4

Location	Chlorine Demand (mg/L)	Segment Apparent Rate Constant (min^{-1})	Cumulative Apparent Rate Constant(min^{-1})
Following Ozonation	2.0		
Filter 2-31 cm	1.6	0.102	0.102
Filter 2-61 cm	1.8	0.026	-0.066
Filter 2-91 cm	1.3	0.061	0.147
GAC 2-10 cm	0.5	0.824	0.824
GAC 2-47 cm	1.2	0.022	-0.501
GAC 2-230 cm	0.4	0.040	0.049
Following Ozonation	1.7		
Filter 4-31 cm	1.4	0.046	0.046
Filter 4-62 cm	1.0	0.054	0.074
Filter 4-91 cm	1.1	0.031	-0.026
GAC 4-23 cm	0.9	0.052	0.052
GAC 4-47 cm	0.6	0.063	0.091
GAC 4-230 cm	0.6	0.013	0.00



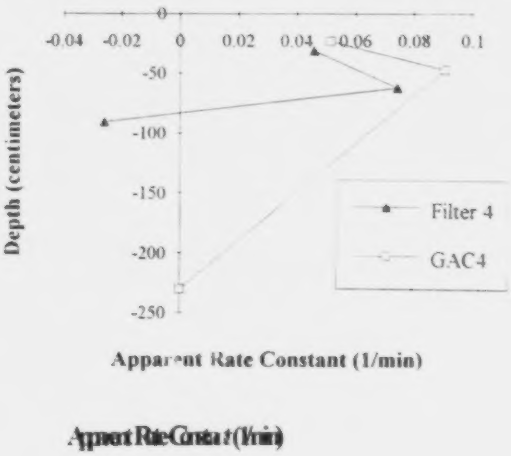


Figure 67: Chlorine Demand Apparent Rate Constants for Streams 2 and 4, Edmonton, Alberta 1992-1993 Study

Laval, Quebec

The Laval, Quebec study measured chlorine demand according to the procedure in Section 3.0. Adequate data were not available for the dual media filtration, however data for two BAC contactors were available in addition to profile data. Figures 68 displays the graphical analysis for BAC contactor 5D. Table 35 summarizes the apparent rate constants and y-intercepts with their 95% confidence intervals for both BAC contactors. The x-intercepts were determined to obtained a minimum achievable concentration. The correlation coefficients were calculated and their level of significance determined.

Table 35
Chlorine Demand Summary of Laval, Quebec Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (mg/L)	y-Intercept* (mg/L.min)	Correlation Coefficient r	EBCT (min)
BAC 2G 10 cm	0.145 ± 0.127	2.5	-0.362± 0.490	0.80†	5.0-7.0
BAC 2G 70 cm	0.054 ± 0.047	2.4	-0.131 ± 0.184	0.80†	13.0-16.0
BAC 2G 130 cm	0.034 ± 0.033	2.4	-0.083 ± 0.729	0.76†	20.0-26.0
BAC 2G Effluent	0.025 ± 0.024	2.5	-0.062 ± 0.091	0.77†	28.0-36.0
BAC 5D 15 cm	0.218 ± 0.380	2.9	-0.622 ± 1.391	0.62‡	5.0-6.0
BAC 5D 80 cm	0.071 ± 0.065	2.7	-0.192 ± 0.237	0.76†	13.0-16.0
BAC 5D 140 cm	0.043± 0.044	2.7	-0.115± 0.160	0.81‡	20.0-26.0
AC 5D Effluent	0.031 ± 0.031	2.7	-0.084 ± 0.112	0.82†	28.0-36.0

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5%

The second stage filtration results for the two BAC contactors analyzed gave apparent first order rate constants of 0.025 and 0.031 min^{-1}, the correlation coefficient for both contactors were significant at the 5% level. Apparent rate constants were determined for three locations along the depth of these contactors. All results were significant at the 5% level, except for two locations along BAC 5D. The x-intercepts were consistent along the depths of the contactors The rate constants for BAC 2G were 0.145 min^{-1}, for a depth of 10 cm, 0.054 min^{-1} for a depth of 70 cm and 0.034 min^{-1} for depth of 130 cm. It was noted that similar trends through the depth of the contactor were observed as with the NVOC and AOC profiles . These results indicate with decreasing removal rates with depth in the contactor. The apparent rate constants were determined per segment along the depth of the contactor. These results are graphed in Figure 69, and indicate that the apparent rate constant decreased with depth, and then slightly increased near the base of the contactor. Although the trend was also noted in the TOC data, it should be noted that for BAC 5D, the 15 cm and 140 cm correlations were not significant at the 5% level, and all depths in BAC 2G were significant at the 5% level.

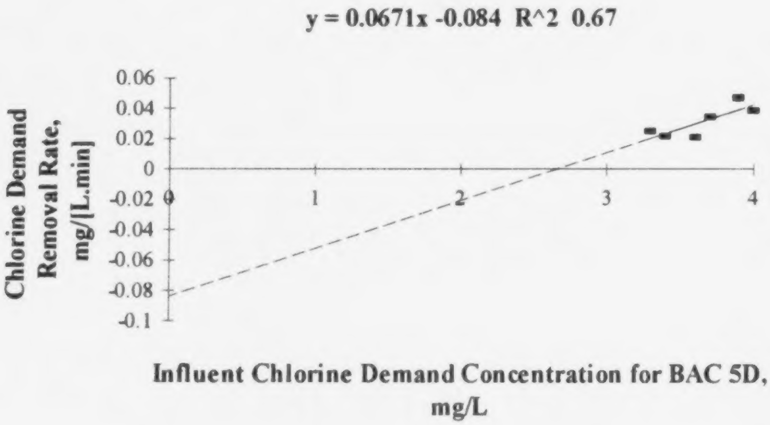


Figure 68: Chlorine Demand Removal Rate vs. Influent Concentration for BAC 5D, Laval, Quebec Study

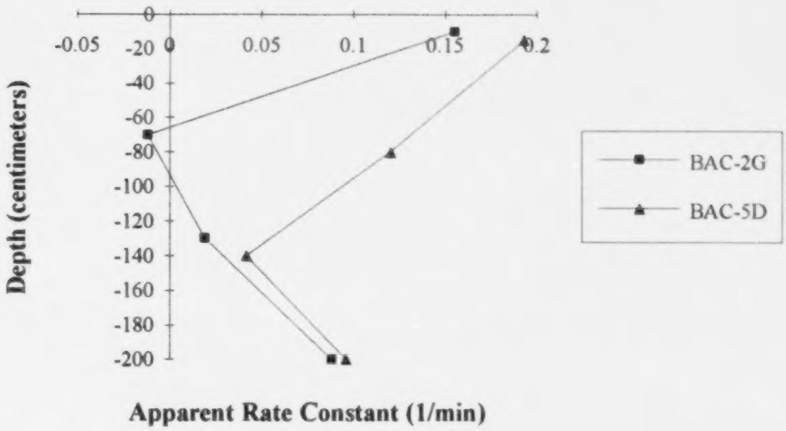


Figure 69: Chlorine Demand Apparent Rate Constant Profile for BAC 2G and 5D.

Discussion and Comparison for Chlorine Demand

In an attempt to discuss and compare the chlorine demand results for the above studies, two graphs were generated. Figure 70 displays the calculated apparent rate constants versus the EBCT and Figure 71 indicates the minimum achievable chlorine demand value versus EBCT. These figures were generated only using apparent rate constants for streams showing significant linearity. In general it appeared that the first stage filtration produced poor linearity, and that better linearity was observed for the second stage filtration. Figure 70 indicates that the apparent rate constant decreases with EBCT. This relationship displays a curve of similar shaped to that found for the HAAFP data.

To better define the non-linear relationship, several equation forms were employed to fit the curve. An equation in the form $x = ae^{-by}$ was found to best define the relationship. The equations were developed through a trial and error process, and a Least Squares analysis was not performed. This curve fit only intended to provide a semi-quantitative basis for comparision. The equation for chlorine demand apparent rate constants and EBCT is:

$$\text{EBCT} = 0.220 \times e^{-(0.08 \times \text{chlorine demand apparent rate constant})}$$

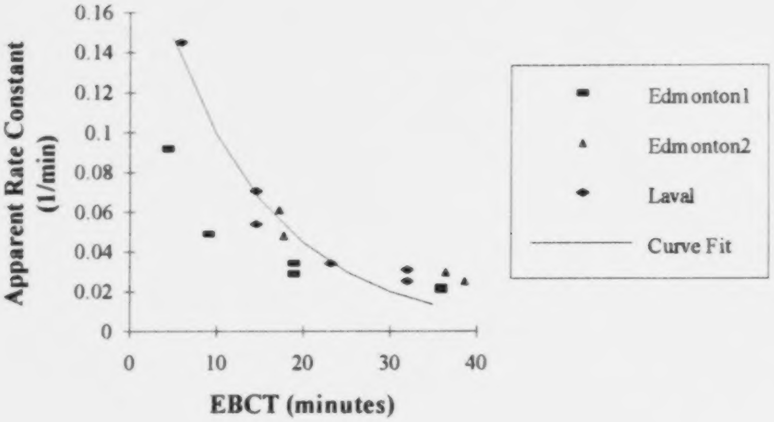


Figure 70: Chlorine Demand Apparent Rate Constant vs. EBCT

Figure 71 indicates that, if all data are considered, there appears to be no apparent relationship between the x-intercept and EBCT. It was noted, however, that the Laval data appeared to produce higher x-intercepts than the Edmonton studies. If only the first Edmonton study is considered, a decrease in the x-intercept with increasing EBCT is seen. The influent chlorine demand for the Laval study ranged from 3.3 to 4.4 mg/L. The influents for the Edmonton 1989-90 study ranged between 3.0 and 19.1 mg/L and the influents for the Edmonton, 1992-93 study ranged between 0.5 and 2.5 mg/L. Since the Edmonton 1992-93 study appears to have the lowest x-intercepts this could be explained by the fact that the influent concentrations were the lowest of the three studies.

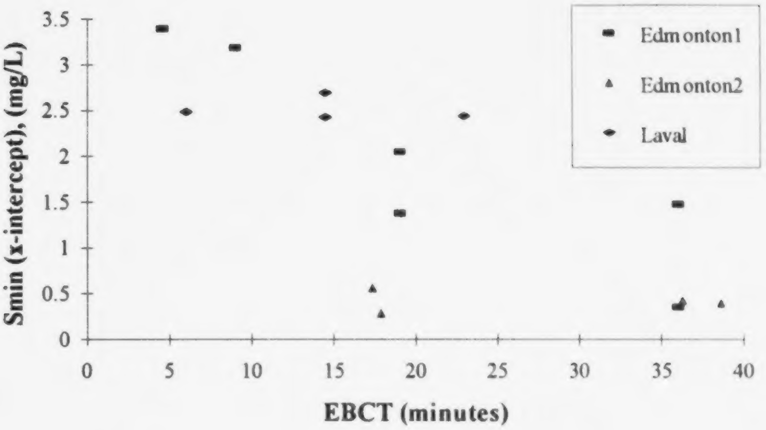


Figure 71: Minimum Achievable Chlorine Demand Concentration vs. EBCT

5.9 Aldehydes

Data were available for the following five aldehydes: formaldehyde, glyoxal, methyl glyoxal, acetaldehyde and propanal. Several studies including Woodbridge, CT, Southern California and Cincinnati, Ohio in addition to Edmonton, Alberta, investigated these compounds and these data were analyzed and the results reported below.

The experimental protocol used for determining aldehydes for the Edmonton study is described in Section 3.0. For the Woodbridge, CT study, the same reference cited for the Edmonton study was given, therefore the method was assumed to be very similar to the Edmonton protocol. The Southern California study also cited the same reference as the above mentioned studies to determine aldehyde concentrations, however minor modifications were conducted to continuously optimize the recovery of all trace aldehydes. The Cincinnati study noted that aldehydes were determined by a method discussed in Miltner et al. (1992). Although these details were unavailable to the author, is was assumed for the purpose of this analysis that the method was similar to that used in the other studies.

5.9.1 Formaldehyde

Edmonton, Alberta Study, 1992-1993

This study determined formaldehyde concentrations for influent and effluent locations from both filters and GAC contactors. The first order apparent rate constants, y-intercepts, x-intercepts and correlation coefficients are reported below in Table 36. All graphical relationships for the filters and GAC contactors are found in Appendix B, Figures B41 and B42.

Table 36
Formaldehyde Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	-0.101± 0.570	-29	-3.010 ± 7.233	0.13‡	5.3-5.5
Filter 2	0.094 ± 0.055	5.2	-0.484± 1.531	0.84	5.5-6.1
Filter 3	0.071± 0.021	3.9	-0.275 ± 0.618	0.99	10.8-11.3
Filter 4	0.072± 0.014	3.2	-0.231 ± 0.041	0.97	8.8-15.7
Filter 5	0.044 ± 0.133	-1.5	0.065 ± 0.473	0.36‡	5.9-5.5
GAC 2	0.036± 0.038	27	-0.985± 1.270	0.65‡	17.2-18.4
GAC 3	0.026 ± 0.010	3.4	-0.087± 0.221	0.96	34.5-38.8
GAC 4	0.005 ± 0.005	1.8	-0.009± 0.214	0.85†	34.5-42.7
GAC 5	0.029 ± 0.024	10	-0.297 ± 0.645	0.96†	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, Filter 1 (chlorinated stream) produced a negative apparent rate constant, and the correlation coefficient was not significant at the 5% level. In addition Filter 5 (non-ozonated stream), yielded a low apparent rate constant and the correlation coefficient was also not significant at the 5% level. The ozonated streams (Filters 2, 3 and 4) produced apparent rate constants ranging from 0.071 to 0.094 min^{-1}. The calculated x-intercepts for these filters ranged between 3.2 and 5.2 μg/L, where the filter adsorber (Filter 4) yielded the lowest x-intercept. All of the ozonated filters indicated good linearity and had correlation coefficients significant at the 1% level. The graphical relationship for Filter 4 is shown in Figure 72.

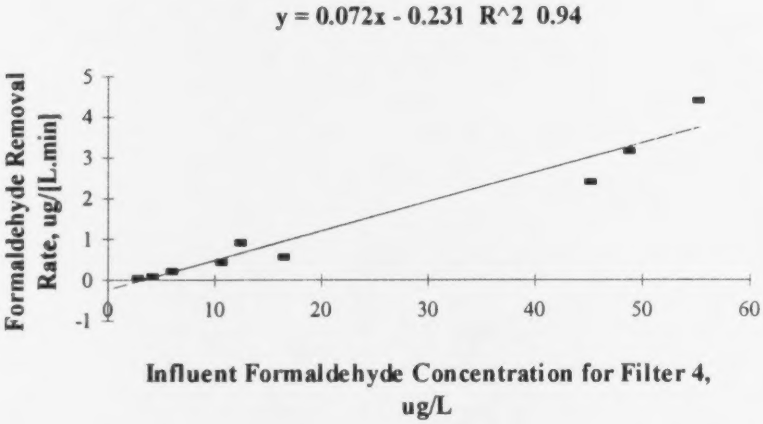


Figure 72: Formaldehyde Removal Rate vs. Influent Concentration for Filter 4, Edmonton, Alberta, 1992-1993

For the second stage filtration, the apparent rate constants ranged from 0.005 to 0.036 min^{-1}. Examination of Figure B42 shows however that relatively few data were available, and that some negative removal rates were calculated for three of the four contactors. The relationship for GAC 2 indicated a higher degree of scatter in the data and the correlation coefficient was not significant at the 5% level. GAC 4 and 5 produced correlation coefficients only significant at the 5% level. The best relationship was observed in GAC 3, and its correlation coefficient of 0.96 was determined to be significant at the 1% level. The x-intercept for GAC 3 was in the same range as the filters. This graphical relationship for GAC 3 is displayed below in Figure 73. It is recognized that the distribution of data points in Figure 73, indicate that the calculated apparent rate constant is based on essentially two data points, therefore reducing its reliability. It was noted that the lowest apparent rate constant was found for GAC 4. This observation has been noted for other compounds and can be explained since this is the stream which employed the filter adsorber in the first stage filtration. Therefore, the filter adsorber tends to remove more formaldehyde in the first stage filtration than the anthracite filters, leaving low concentrations to be removed in the second stage filtration.

In general it was observed that the apparent rate constants were dependent on the hydraulic loading rate. In addition streams with a statistically significant correlation coefficient produced positive x-intercepts indicating a minimum concentration which could be achieved biologically. This concentration is quite low, on the order of a few μg/L.

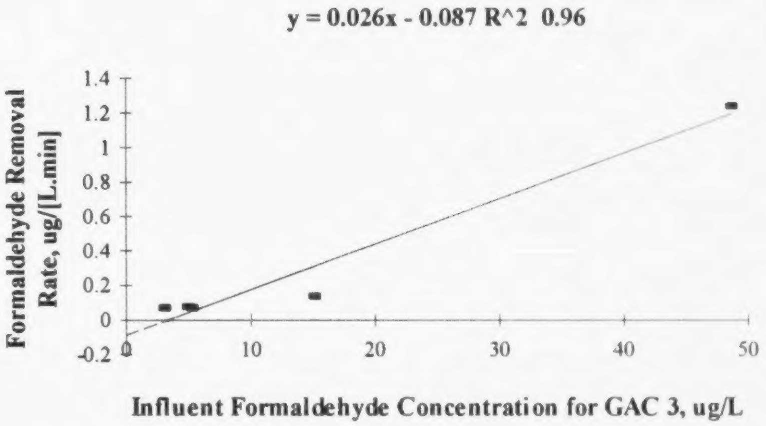


Figure 73: Formaldehyde Removal Rate vs. Influent Concentration for GAC 3, Edmonton, Alberta 1992-1993

Woodbridge, CT Study

This study employed only a first stage filtration step and reported the influent and effluent formaldehyde concentrations. This study, as mentioned in other sections, doubled the hydraulic loading rate for two days during the study which represents up to 50% of the data points in some filters. These data were analyzed using the designated EBCT and the results produced relationships with more scatter in the data than when the data were analyzed with the same EBCT throughout the study. However, the results reported below in Table 37 are from the analysis using the exact EBCT on the day of sampling.

Table 37

Formaldehyde Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.080 ± 0.130	-1.7	0.137± 1.102	0.64‡	6.2-12.2
Filter 2	0.238 ± 0.345	6.0	-1.422± 1.178	0.96†	6.2-12.2
Filter 3	0.103 ± 0.118	0.6	-0.064 ± 0.145	0.85‡	6.2-12.2
Filter 4	0.112± 0.030	0.7	-0.074 ± 0.041	0.99	6.2-12.2
Filter 5	0.096 ± 0.096	0.2	-0.021 ± 0.121	0.81‡	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

The results show that for the ozonated GAC/Sand filters (Filter 1 and 2) the apparent rate constants varied greatly. The correlation coefficient for Filter 1 was not significant at the 5% level, however Filter 2 was only significant at the 5% level. For the non-ozonated streams, Filter 4 produced the only correlation coefficient significant at the 1% level. The apparent rate constant for stream 4 was 0.112 min^{-1} and the x-intercept was 0.66 µg/L. The graphical relationship for Filter 4 is shown below in Figure 74.

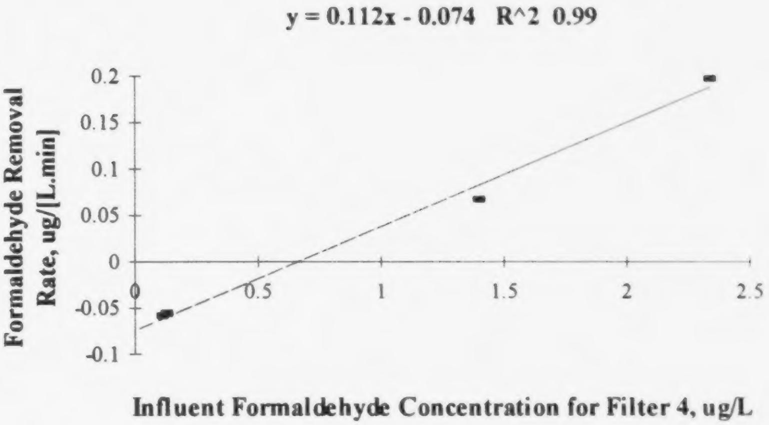


Figure 74: Formaldehyde Removal Rate vs. Influent Concentration for Filter 4, Woodbridge, CT Study

Southern California Study

This study consisted of two phases which employed a different water source for each phase. The first phase was designed to investigate hydraulic loading rate, where the second phase focused on type of media. This study only employed a first stage filtration step. The apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 38. The graphical relationships of all the filters in these phases can be found in Appendix B, Figure B44 and B45. Of note is the fact that the EBCTs used in this study were very short (maximum 4.2 minutes).

Table 38

Formaldehyde Summary for Southern California Study

Stream (Phase)	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
FE1(I)	0.178 ± 0.0410	-3.0	0.534± 0.541	0.89	4.2
FE3(I)	0.197 ± 0.224	-11.6	2.289± 2.982	0.37‡	2.1
FE5(I)	0.089 ± 0.370	-60.7	5.403± 4.925	0.11‡	1.4
FE2(I)	0.702 ± 0.342	1.2	-0.853± 5.207	0.79	1.4
FE4(I)	0.762 ± 0.278	1.5	-1.164± 4.235	0.87	1.4
FE6(I)	0.209 ± 0.095	-1.7	0.351± 1.453	0.81	4.2
FE1(II)	0.228 ± 0.132	-1.7	0.381 ± 1.237	0.55	2.1
FE3(II)	0.328± 0.063	-2.6	0.859 ± 0.593	0.89	2.1
FE5(II)	0.327 ± 0.068	-2.8	0.915 ± 0.643	0.88	2.1

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For phase I, the anthracite/sand filters FE1 operated an EBCT of 4.3 minutes and produced an apparent rate constant of 0.178 min^{-1}. The correlation coefficient for FE1 (the highest EBCT) was significant at the 1% level. The graphical relationship for FE1 is displayed in Figure 75. Filters FE3 and FE5 (which were all operated at different EBCTs) produced apparent rate constants ranging from 0.089 to 0.197 min^{-1}. It was also noted that the data for FE3 and FE5 could be separated into to subsets, representing a different apparent rate constant for a given season. The correlation coefficients were not significant at the 5% level for FE3 and FE5, however the GAC/sand filters (FE2, FE4 and FE6) all showed good linearity and correlation coefficients were all significant at the 1% level. The apparent rate constants for these streams varied according to EBCT. It should be noted that FE4 and FE6 contained spent GAC.

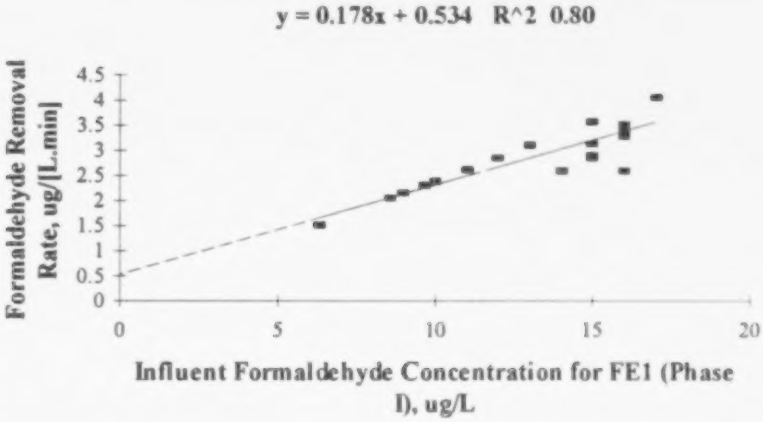


Figure 75: Formaldehyde Removal Rate vs. Influent Concentration for FE1 (Phase I), Southern California Study

For Phase II, the filters were all hydraulically loaded at the same rate. The anthracite filter (FE1) produced the lowest apparent rate constant and showed the least linearity. The GAC filters (FE3 and FE5) produced approximately the same apparent rate constant and correlation coefficient. The x-intercepts for all Phase I and II filters showing significant linearity were very low, ranging between -3.0 to 1.5 μg/L. These results also indicate that apparent rate constants are dependent on EBCT and that better linearity was observed in GAC filters at all EBCTs and in anthracite filters operated at a higher EBCT.

Discussion and Comparison for Formaldehyde

In an attempt to discuss and compare the formaldehyde results for the above studies, Figure 76 was generated to display the relationship between apparent rate constant and EBCT. This figure was generated only using apparent rate constants for streams showing significant linearity. In general it appeared that the first stage filtration produced better linearity than the second stage filtration. It was noted that again the apparent rate constants appeared to be dependent on EBCT and Figure 76 indicates that a non linear relationship exists between apparent rate constant and EBCT. The shape of this curve is different than that of curves generated for other parameters. Figure 76 displays a very steep slope which begins to flatten out at approximately 5 minutes. This characteristic confirms what is known about aldehydes, being that these low molecular weight compounds are more readily biodegradable than other parameters of concern. The shape of this curve indicates that shorter EBCTs are as effective in removing formaldehyde as longer EBCTs.

To better define the non-linear relationship, several equation forms were employed to fit the curve. An equation in the form $x = ae^{-by}$ was found to best define the relationship. The equations were developed through a trial and error process, and a Least Squares analysis was not performed. This curve fit only intended to provide a semi-quantitative basis for comparision. The equation for formaldehyde apparent rate constants and EBCT is:

$$\text{EBCT} = 1.20 \times e^{-(0.35 \times \text{formaldehyde apparent rate constant})}$$

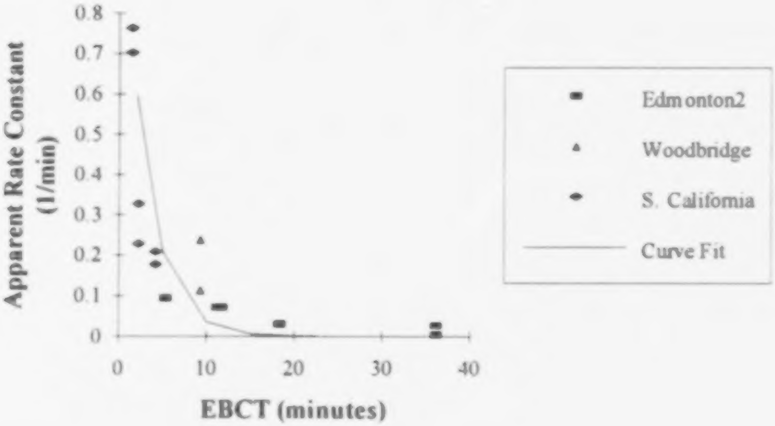


Figure 76: Formaldehyde Apparent Rate Constants vs. EBCT

The x-intercepts were not plotted against EBCT since no obvious trend was noted in the data. It was observed that especially in the shorter EBCT filters, negative x-intercepts were determined indicating that for practical purposes, all influent formaldehyde could be removal biologically.

5.9.2 Methyl Glyoxal

Edmonton, Alberta Study, 1992-1992

Methyl glyoxal was reported for influent and effluent locations for the filters and GAC filters. The apparent first-order rate constants, x-intercepts, y -intercepts and correlation coefficients are reported in Table 39. The graphical relationship for all filters and GAC contactors is found in Appendix B, Figures B46 and B47.

Table 39

Methyl Glyoxal Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.002± 0.003	0.50	-0.001 ± 0.016	0.50‡	5.3-5.5
Filter 2	0.005 ± 0.010	-0.20	0.001± 0.081	0.39‡	5.5-6.2
Filter 3	-0.024± 0.063	0.46	0.011 ± 0.313	0.58‡	10.8-11.3
Filter 4	0.007± 0.011	0.02	-1.4e-4± 0.075	0.49‡	8.8-15.7
GAC 2	0.005± 0.006	0.20	-0.001± 0.038	0.31‡	17.2-18.4
GAC 3	0.008 ± 0.019	1.0	-0.008± 0.127	0.80‡	34.5-38.8
GAC 4	0.0002±0.004	0.05	-9.1e-5± 0.003	0.40‡	34.5-42.7

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

The results obtained for both first and second stage filtration resulted in very low apparent rate constants and none of the correlation coefficients were significant at the 5% level. The poor linearity is shown in Figure 77 for Filter 2. It was observed that both the first and second stage filtration had little or no effect in reducing influent concentrations for this study.

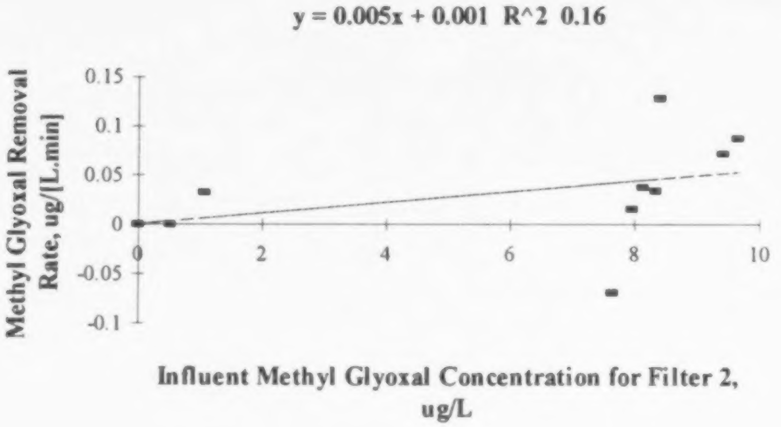


Figure 77: Methyl Glyoxal Removal Rate vs. Influent Concentration for Filter 2, Edmonton, Alberta, 1992-1993

Woodbridge, CT Study

This study reported methyl glyoxal for influent and effluent locations for five filters. The calculated apparent rate constants, x-intercepts, y-intercepts, and correlation coefficients are shown in Table 40. These results were determined using the individual hydraulic loading rates on each sampling day. It will be recalled that these rates were doubled on two occasions. The graphical relationships for these filters are displayed in Appendix B, Figure B48.

Table 40

Methyl Glyoxal Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.108 ± 0.158	0.16	-0.017± 0.449	0.69‡	6.2-12.2
Filter 2	0.144 ± 0.158	1.2	-0.171± 0.434	0.86‡	6.2-12.2
Filter 3	0.321 ± 0.294	0.16	-0.051 ± 0.052	0.90†	6.2-12.2
Filter 4	0.089± 0.201	-0.02	0.002 ± 0.035	0.80‡	6.2-12.2
Filter 5	0.082 ± 0.161	0.01	-0.001 ± 0.175	0.58‡	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

The results produced a range of apparent rate constants and for all filters except Filter 3, the correlation coefficients were not significant at the 5% level. Filter 3 has an apparent rate constant of 0.321 min^{-1}, and a correlation coefficient of 0.90. The graphical relationship for Filter 3 is shown in Figure 78.

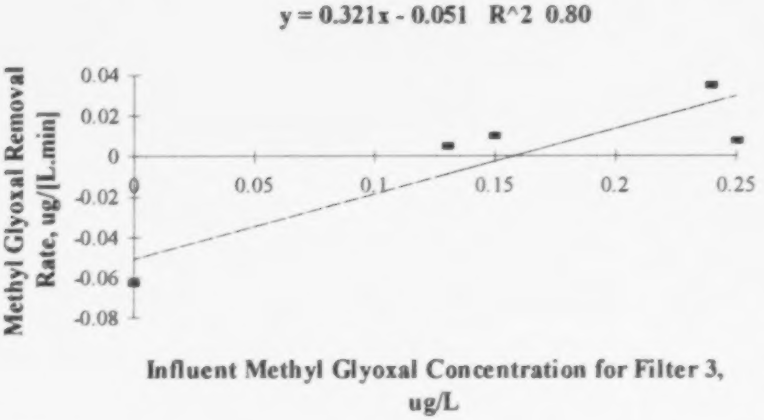


Figure 78: Methyl Glyoxal Removal Rate vs. Influent Concentration for Filter 3, Woodbridge, CT Study

Southern California Study

This study reported methyl glyoxal for the phase I study only. This phase employed six filters containing anthracite, virgin GAC or spent GAC overlying sand. The filters were hydraulically loaded at three different rates. The calculated apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are displayed in Table 41. The graphical relationships for these filters are displayed in Appendix B, Figure B49.

Table 41
Methyl Glyoxal Summary for Southern California Study

Stream (Phase)	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
FE1(I)	0.170 ± 0.075	-1.1	0.179± 0.559	0.69	4.2
FE3(I)	0.044 ± 0.240	-39	1.732± 1.788	0.08‡	2.1
FE5(I)	0.096 ± 0.262	18	1.822± 1.949	0.15‡	1.4
FE2(I)	0.672 ± 0.294	1.5	-1.033± 2.452	0.79	1.4
FE4(I)	0.612 ± 0.210	0.38	-0.230± 1.757	0.88	1.4
FE6(I)	0.213 ± 0.053	0.22	0.047± 0.444	0.92	4.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

For the anthracite filters (FE1, FE3 and FE5) the apparent rate constants ranged between 0.044 and 0.190 min^{-1}. Filters FE1 and FE3 were observed to have a lot of scatter in the data and the correlation coefficients were not significant at the 5% level. Filter FE1 indicated slightly better linearity and had a correlation coefficient of 0.69 which was significant at the 1% level. The GAC filters indicated better linearity and all calculated correlation coefficients were significant at the 1% level. The apparent rate constants ranged between 0.213 and 0.612 min^{-1}, and were dependent on hydraulic loading rate. The graphical relationship is shown below in Figure 79 for FE6. The removal of methyl glyoxal was not suspected to be by adsorption, due to the high methyl glyoxal removal rate by the spent GAC filters (FE2 and FE4).

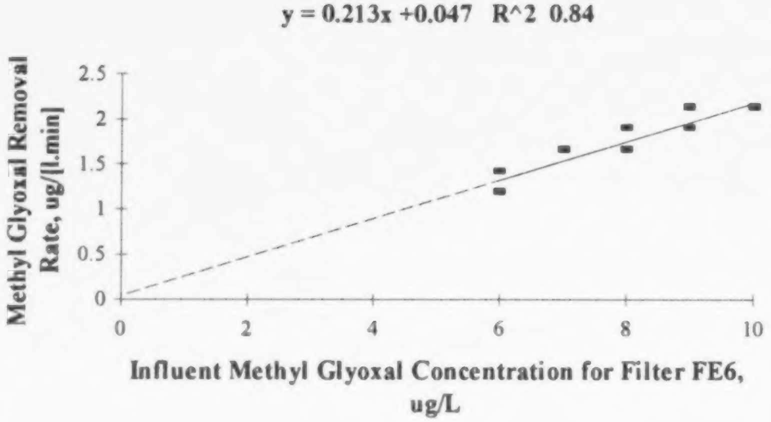


Figure 79: Methyl Glyoxal Removal Rate vs. Influent Concentration for FE 6, Southern California Study

Cincinnati, Ohio Study

This study reported influent and effluent methyl glyoxal concentrations for eight filters. All the filters were operated at the same hydraulic loading rate. The apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are reported in Table 42. The graphical relationships for all filters are found in Appendix B, Figure B50.

Table 42
Methyl Glyoxal Summary for Cincinnati, Ohio Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.045 ± 0.062	8.5	-0.382 ± 0.438	0.23‡	10.32
Filter 2	0.040 ± 0.026	-4.4	0.175 ± 0.234	0.57	10.43
Filter 3	0.100 ± 0.004	0.2	-0.018 ± 0.031	1.00	9.82
Filter 4	0.094 ± 0.001	0.04	-0.004 ± 0.011	1.00	10.47
Filter 5	0.098 ± 0.002	0.11	-0.011 ± 0.016	1.00	10.04
Filter 6	0.086 ± 0.010	0.03	-0.003 ± 0.011	0.99	11.49
Filter 7	0.089 ± 0.002	0.13	-0.012 ± 0.015	1.00	11.26
Filter 8	0.096 ± 0.002	0.03	-0.003 ± 0.016	1.00	10.29

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

The results for Filter 1 (chlorinated stream) and Filter 2 (chlorinated backwash) showed a lot of scatter in the data for all the filters. The remaining filters consisting of either anthracite/sand, GAC/sand or only sand produced similar apparent rate constants ranging from 0.086 to 0.100 min^{-1}. The correlation coefficients were all significant at the 1% level. It was noted that close to 100% of the influent methyl glyoxal was removed in all these filters, and that the linearity was almost perfect. This linear relationship is displayed in Figure 80 for Filter 7.

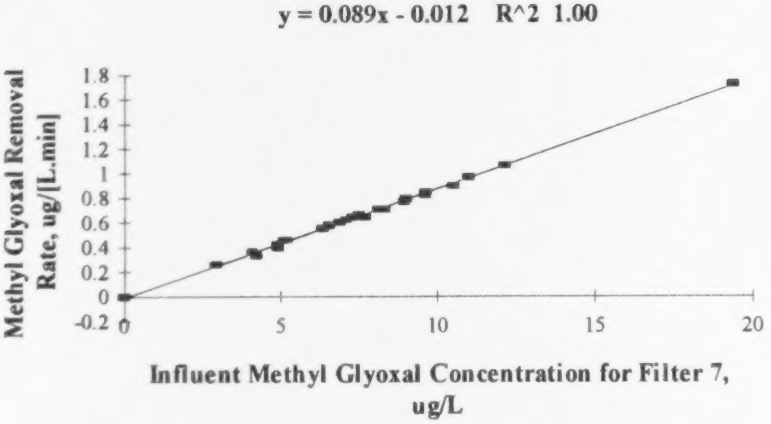


Figure 80: Methyl Glyoxal Removal Rate vs. Influent Concentration for Filter 7, Cincinnati, Ohio Study

Discussion and Comparison for Methyl Glyoxal

In an attempt to compare the results from the above studies Figure 81 was generated. Edmonton data were not included, because none of the correlation coefficients were significant. The graph indicates no apparent relationship between apparent rate constant and EBCT. The results produced from these four studies were variable. The Edmonton study showed almost no removal from first and second stage filtration. The Woodbridge and Southern California studies produced results showing a lot of scatter in the data. The Cincinnati study produced results showing perfect correlation and complete removal of the influent methyl glyoxal. It is suspected that there may have been differences in experimental or sampling protocols which contributed to this variability.

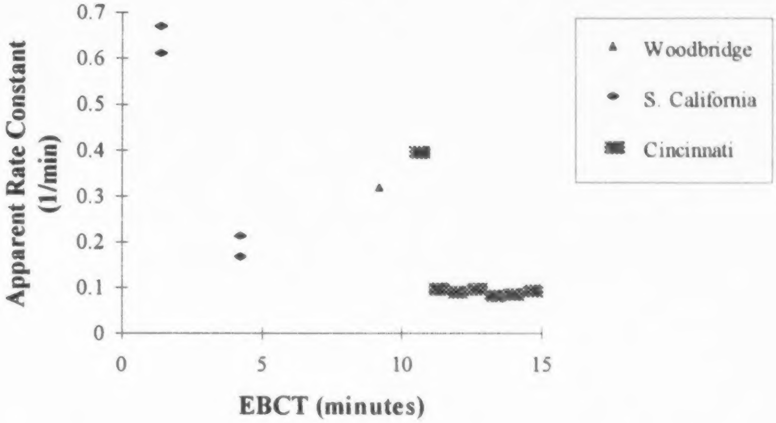


Figure 81: Methyl Glyoxal Apparent Rate Constant vs. EBCT

5.9.3 Glyoxal

Edmonton, Alberta Study, 1992-1993

Glyoxal was reported for influent and effluent locations for the filters and GAC contactors. The apparent first-order rate constants, x-intercepts, y -intercepts and correlation coefficients are reported in Table 43. The graphical relationships for all filters and GAC contactors are found in Appendix B, Figures B51 and B52.

Table 43

Glyoxal Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.179± 0.022	5.1	-0.917 ± 0.612	0.98	5.3-5.5
Filter 2	0.065 ± 0.004	5.7	-0.371± 0.220	0.99	5.5-6.1
Filter 3	-0.057± 0.102	0.94	0.054 ± 0.568	0.61	10.8-11.3
Filter 4	0.025± 0.001	4.6	-0.116 ± 0.079	0.99	8.8-15.7
Filter 5	0.076± 0.792	13	-1.012 ± 2.609	0.10‡	5.9-5.5
GAC 2	0.051± 0.005	5.4	-0.277± 0.181	0.99	17.2-18.4
GAC 3	0.022 ± 0.013	1.6	-0.036± 0.152	0.89	34.5-38.8
GAC 4	-0.004±4.0e-4	5.5	0.022± 0.014	0.90	34.5-42.7
GAC 5	0.028 ± 0.003	2.4	-0.067 ± 0.105	0.99	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

The results obtained for this parameter are not as good as they appear. For most of the filters and GAC contactors, the correlation coefficients are all significant at the 1% level indicating excellent linearity in all the filters and GAC contractors. Observation of the actual plots revealed that most of the data points show no removal, and one point indicates a high influent and subsequent removal. This data distribution has led to almost perfect linearity, although in essence only two data points exist. An example of this phenomenon is shown in Figure 82 for Filter 2. These results are not considered useful for comparison due to the nature of the data.

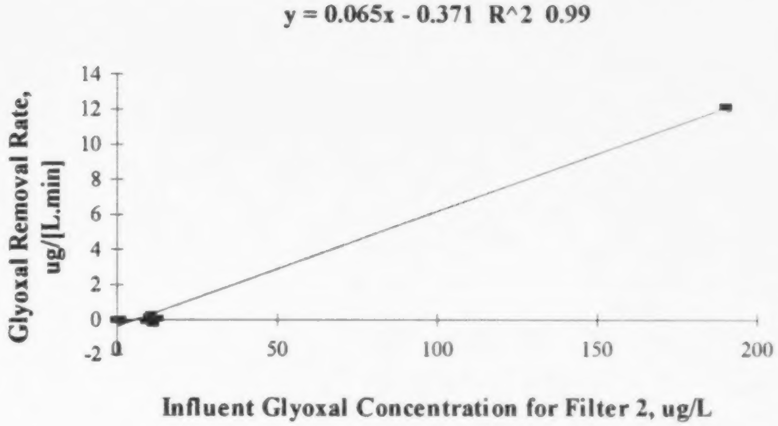


Figure 82: Glyoxal Removal Rate vs. Influent Concentration for Filter 2, Edmonton, 1992-1993 Study

Woodbridge, CT Study

This study reported methyl glyoxal for influent and effluent locations for five filters. The calculated apparent rate constants, x-intercepts, y-intercepts, and correlation coefficients are shown in Table 44. These results were determined using the individual hydraulic loading rates on each sampling day. It should be recalled that this rate was doubled on two occasions.

Table 44
Glyoxal Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient R	EBCT (min)
Filter 1	0.069 ± 0.056	-1.4	0.093± 0.315	0.75†	6.2-12.2
Filter 2	0.062 ± 0.060	-0.1	0.026± 0.362	0.86†	6.2-12.2
Filter 3	-0.095 ± 0.320	0.02	0.019 ± 0.093	0.38‡	6.2-12.2
Filter 4	0.007± 0.379	1.6	-0.011 ± 0.115	0.05‡	6.2-12.2
Filter 5	-0.009 ± 0.203	0.1	0.001 ± 0.054	0.06‡	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

The results produced varying apparent rate constants for all filters, The correlation coefficients for Filters 3, 4, and 5 were not significant at the 5% level. The two ozonated filters showed better linearity and had correlation coefficients significant at the 5% level. The apparent rate constants for these filters were 0.062 and 0.069 min^{-1}. The graphical relationship for Filter 1 is shown in Figure 83. The graphical relationships of all the filters in these phases can be found in Appendix B, Figure B54.

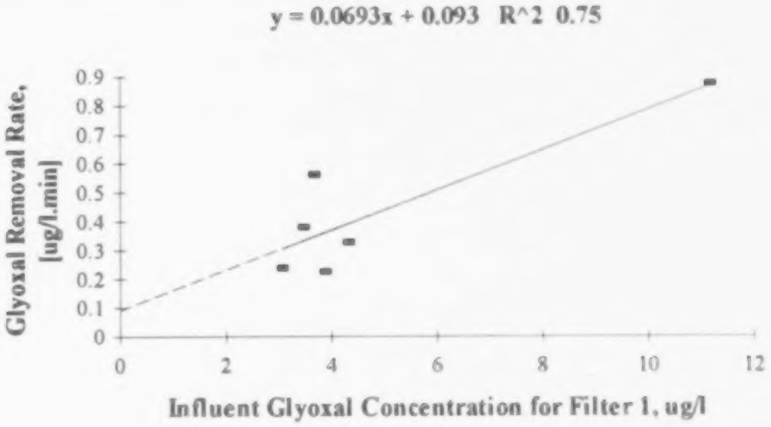


Figure 83: Glyoxal Removal Rate vs. Influent Concentration for Filter 1, Woodbridge, CT Study

Southern California Study

This study consisted of two phases which employed a different water source for each phase. The first phase was designed to investigate the hydraulic loading rate, where the second phase focused on type of media. This study only employed a first stage filtration step and the apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 45. The graphical relationships of all the filters in these phases can be found in Appendix B, Figures B55 and B56

Table 45
Glyoxal Summary for Southern California Study

Stream (Phase)	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
FE1(I)	0.056 ± 0.096	-15.9	0.888± 0.541	0.10‡	4.2
FE3(I)	-0.057 ± 0.144	38.3	2.181± 1.324	0.17‡	2.1
FE5(I)	-0.095 ± 0.051	27.5	2.617± 1.427	0.31‡	1.4
FE2(I)	0.829 ± 0.845	4.4	-3.661± 9.122	0.49‡	1.4
FE4(I)	0.840 ± 0.686	3.4	-2.875± 7.407	0.57†	1.4
FE6(I)	0.278 ± 0.039	1.6	-0.442± 0.422	0.97	4.2
FE1(II)	0.330 ± 0.144	0.5	-0.167 ± 0.616	0.66	2.1
FE3(II)	0.305± 0.112	0.6	0.193 ± 0.477	0.73	2.1
FE5(II)	0.363 ± 0.117	0.4	0.139 ± 0.501	0.77	2.1

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

For the phase I study all the filters accept FE4 and FE6 were not significant at the 5% level. Only FE6 indicated good linearity in this phase. For Phase II, all the filters produced similar apparent rate constants, despite EBCT and all were significant at the 1% level, with the best linearity shown in the GAC filters. It was noted in this phase that the linear relationship appeared to produce two or more different apparent rate constants depending on the season or point in the study (Figure B56). Further investigation found that data taken during the end of the study indicated almost complete removal of glyoxal. This would indicate that the biofilm was better able to remove glyoxal near the end of the study. The data provided reported concentrations very early in the operational life of the filters, therefore, the first two weeks of data was not used in this analysis, to account for biofilm development. These results would indicate that different media types may require longer periods of time to develop a substantial biofilm. In addition, it was observed that for other parameters measured in the Southern California study, a higher recent removal was obtained early in the study than for glyoxal. Therefore, it may take longer for necessary organisms in the biofilm to remove glyoxal. The graphical relationship for FE3 (Phase II) is shown in Figure 84

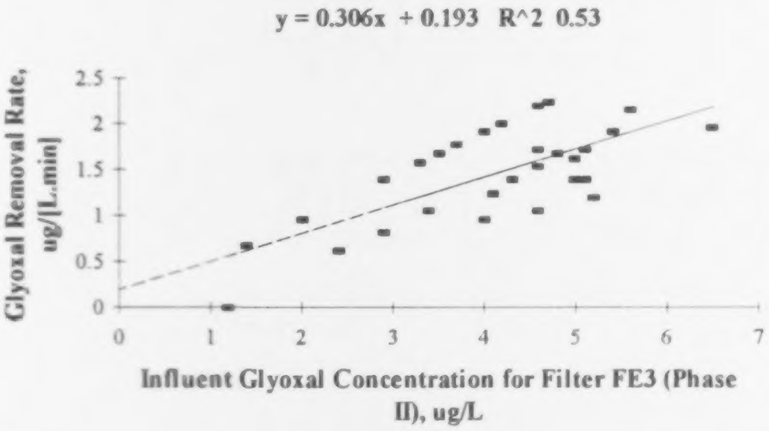


Figure 84: Glyoxal Removal Rate vs. Influent Concentration for FE3 (Phase II), Southern California Study

Discussion and Comparison for Glyoxal

The analysis of the data from the Edmonton and Woodbridge studies indicated that the first order relationship fit poorly. Only the Southern California study produced a good fit. From the results it would appear that the apparent rate constants were dependent on EBCT, however only the filters containing GAC produced good linearity which could indicate that adsorption accounted for the removal of glyoxal. A recent study by Weinberg et al, (1993), stated that glyoxal appeared to be more difficult to remove through biological mediation than formaldehyde and acetaldehyde. An additional reference stated that glyoxal in dilute aqueous solution kept at 20°C in light could be spontaneously oxidized into glyoxylic acid and probably formaldehyde (Jarret et al. 1986). The latter fact could indicate that differences in experimental protocol could greatly effect the measurement of glyoxal and help explain the varying results for these studies.

5.9.4 Acetaldehyde

Edmonton, Alberta Study, 1992-1993

Acetaldehyde was reported for influent and effluent locations for filters and GAC contactors. The calculated apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are reported in Table 46. The graphical relationships for all the filters and GAC contactors are shown in Appendix B, Figures B57 and B58 .

Table 46

Acetaldehyde Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.074± 0.090	1.0	-0.073 ± 0.602	0.56‡	5.3-5.5
Filter 2	0.057 ± 0.089	-0.1	0.008± 0.293	0.43‡	5.5-6.1
Filter 3	0.028± 0.028	-0.3	0.001 ± 0.059	0.87‡	10.8-11.3
Filter 4	0.087± 0.028	0.7	-0.060 ± 0.078	0.92	8.8-15.7
Filter 5	-0.042± 0.050	1.4	0.060 ± 0.179	0.64‡	5.9-5.5
GAC 2	0.046± 0.009	0.4	-0.017± 0.019	0.97	17.2-18.4
GAC 3	0.013 ± 0.001	0.4	-0.005± 0.003	1.00	34.5-38.8
GAC 4	0.017± 0.029	0.9	-0.016± 0.024	0.44‡	34.5-42.7
GAC 5	0.046 ± 0.024	0.6	-0.027 ± 0.034	0.89	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration the only filter to produce a correlation coefficients significant at the 1% level was the filter adsorber. The second stage filtration produced correlation coefficients all significant at the 1% level, except for GAC 4. These results may indicate that removal of acetaldehyde was by adsorption. Huck et al. (1990) showed little removal of acetaldehyde through a biological process. The graphical relationship for Filter 4 is shown in Figure 85. The x-intercepts for all significant correlation coefficients were positive indicating a minimum concentration which could be achieved.

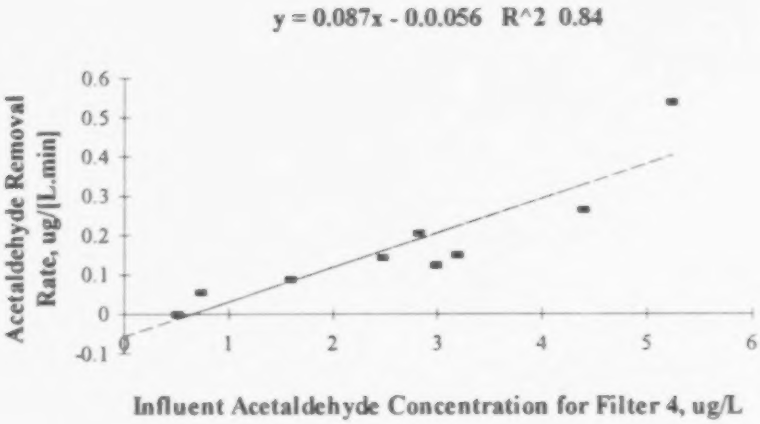


Figure 85: Acetaldehyde Removal Rate vs. Influent Concentration for Filter 4, Edmonton, Alberta 1992-1993 Study

Woodbridge, CT Study

This study determined acetaldehyde for the influent and effluent locations for five filters. The calculated apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 47. All filters except Filter 3 and 5 produced results not significant at the 5% level. Filter 5 produced a good linear relationship and had a correlation coefficient of 0.95. The graphical relationship for Filter 5 is shown in Figure 86.

Table 47
Acetaldehyde Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.172 ± 0.199	0.8	-0.145± 0.364	0.85‡	6.2-12.2
Filter 2	0.178 ± 0.088	0.1	-0.016± 1.182	0.67‡	6.2-12.2
Filter 3	0.160 ± 0.088	0.1	-0.011 ± 0.018	0.98†	6.2-12.2
Filter 4	-0.627± 1.594	0.07	0.413 ± 0.046	0.46‡	6.2-12.2
Filter 5	0.175 ± 0.117	0.06	-0.010 ± 0.041	0.95†	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

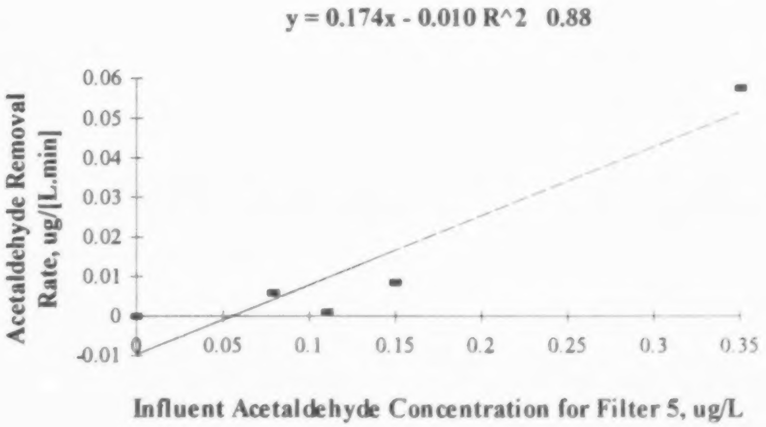


Figure 86: Acetaldehyde Removal Rate vs. Influent Concentrations for Filter 5, Woodbridge, CT Study

Discussion and Comparison for Acetaldehyde

The apparent rate constants for acetaldehyde appear also to be dependent on EBCT, however, for the Edmonton study the first stage filtration produced correlations that were not statistically significant, except of the filter adsorber (GAC/sand). Although this could indicate that removal was achieved through adsorption, it is suspected that a secondary filtration stage may be required to achieve high acetaldehyde removal.

5.9.5 Propanal

Edmonton, Alberta Study, 1992-1993

The final aldehyde analyzed in the Edmonton study was propanal. These apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 48. For the first stage filtration, all filters except Filter 5 (non-ozonated) produced correlation coefficients significant at least at the 5% level. The apparent rate constants for these filters ranged between 0.033 and 0.106 min^{-1}. For the second stage filtration the correlation coefficients were not significant at the 5% level except for GAC 5. Examination of Figure B61 indicated that in many cases little removal was achieved in the BAC contactors. These results would indicate that propanal is mostly removed in the first stage filtration and for non-ozonated streams a second filtration step is required. The graphical relationship for Filter 2 is shown in Figure 87. The plots for all filters and BAC contactors are found in Appendix B, Figures B60 and B61.

Table 48

Propanal Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.106± 0.055	0.99	-0.188 ± 0.327	0.81	5.3-5.5
Filter 2	0.048 ± 0.041	-0.14	-0.082± 0.176	0.69†	5.5-6.1
Filter 3	0.054± 0.024	-0.25	-0.071 ± 0.092	0.91	10.8-11.3
Filter 4	0.033± 0.025	0.69	-0.048 ± 0.098	0.74†	8.8-15.7
Filter 5	-0.016± 0.083	1.42	-0.027 ± 0.223	0.19‡	5.9-5.5
GAC 2	0.033± 0.156	037	-0.028± 0.501	0.19‡	17.2-18.4
GAC 3	0.020± 0.024	0.37	-0.017± 0.046	0.76‡	34.5-38.8
GAC 4	-0.040± 0.078	0.94	0.043± 0.239	0.39‡	34.5-42.7
GAC 5	0.055 ± 0.023	059	-0.045 ± 0.059	0.92	17.3-17.3

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

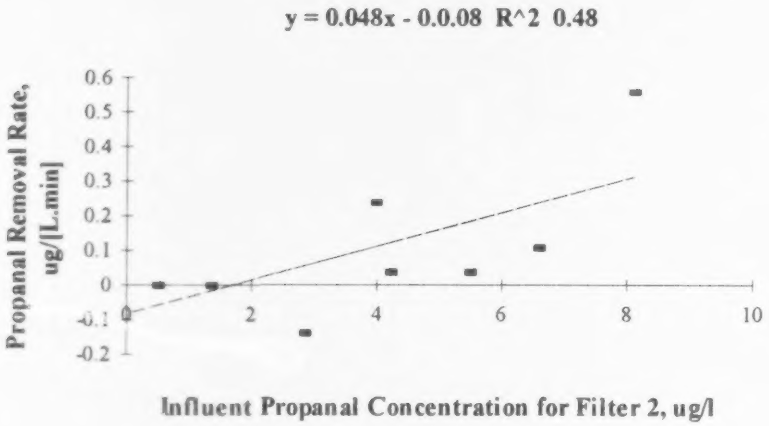


Figure 87: Propanal Removal Rate vs. Influent Concentration for Filter 2, Edmonton, Alberta 1992-1993 Study

CHAPTER 6

DISCUSSION AND COMPARISON OF VARIOUS PARAMETERS

This chapter will discuss and compare the parameters within a specific class (i.e. chlorinated by-product precursors) and also compare results among the different classes for compounds.

6.1 Biodegradable Organic Matter (BOM)

The parameters which fit into the BOM group were nonvolatile organic carbon (NVOC), assimilable organic carbon (AOC) and biodegradable organic carbon (BDOC). It was found that in all studies for every parameter, the apparent rate constants spanned the same range, approximately 0.02 to 0.120 min^{-1}. As noted in the comparisons among studies it was found that for NVOC, the apparent rate constants were independent of hydraulic loading rate for the first stage filtration, whereas the second stage filtration was dependent on hydraulic loading rate. For AOC it was found that rate constants for both first and second stage filtration were dependent on hydraulic loading rate. Only a second stage filtration for BDOC was available and it was found that the rate constants were also independent of hydraulic loading rate. Profile data for all of these studies, where cumulative apparent rate constants were calculated, confirmed the above observations when results were statistically significant. When apparent rate constants for each segment along the filters were determined, it indicated that for the first stage filtration, apparent rate constants were higher at the top of the filter and decreased with depth as expected; however, some increases were also observed. In the second stage filtration, the segment apparent rate constants were very high at the top of the column followed by a sharp decrease, and a slight further decrease with depth beyond this point. The apparent rate constants also showed increases with depth but not as often as seen in the first stage filters. For the BOM parameters the type of media appeared to have no obvious effects on the apparent rate constants for both first and second stage filtration.

In general there were similar observations among these three parameters. It was observed that the pre-ozonated streams indicated the better linearity, where the worst linearity was observed in the chlorinated streams, followed by non-ozonated streams. Typically the apparent rate constants for the chlorinated and non-ozonated streams were lower than for the ozonated streams. It was observed that the second stage filtration indicated better linearity than the first stage filtration. This could be due to more frequent backwashing for the first stage filters, because these filters were backwashed every 24 hours in most studies and the GAC contactors were only backwashed once a week in most cases. The more frequent backwashing could have removed some of the biofilm, which would decrease the amount of substrate removed. A second explanation for the improved linearity at the second stage could be that the first stage filtration receives intermittent higher and more variable substrate concentrations, whereas the second stage filtration would receive more nearly constant substrate concentrations. It was noted that for the Edmonton 1989-1990 study different ozone doses were used in different streams, and generally, the lower ozone dose produce results showing better linearity than the higher ozone dose. It is known that for the Edmonton, 1992-1993 study, the ozone dose did vary significantly due to problems with the ozone generating equipment. It was observed that better linearity was noted in the earlier Edmonton study, which could be explained by the more consistent ozone dosages. An additional difference between these two studies was the use of an air scour step during backwashing of the first stage filters for the Edmonton 1992-1993 study. This action could potentially aid the removal of biofilm from filter media, and lead to less consistent removals.

6.2 Chlorinated by-product precursors

The parameters included in this class of compounds were dichloroacetic acid formation potential (DCAAFP), trichloroacetic acid formation potential, chloral hydrate formation potential (CHFP), adsorbable organic halogen formation potential (AOXFP), trihalomethane formation potential (THMFP) and chlorine demand (CD).

DCAAFP and TCAAFP produced very similar results. It was observed that for both of these parameters, good linearity was observed at the first stage filtration step and better linearity was observed at the second stage filtration. The first stage filters showing the poorest linearity were the chlorinated and non-ozonated streams. The best linearity for the first stage filtration was noted in GAC/sand filters suggesting that adsorption may play some role. However, the apparent rate constants were similar for filters with anthracite/sand and GAC/sand. A non-linear relationship between apparent rate constants and EBCT was observed for these two parameters, and the same relationship was observed in the x-intercepts, where the x-intercepts and apparent rate constants decreased non-linearly with increasing EBCT. The relationship between the rate constants and EBCT is discussed later in this chapter. It was noted in the profile data for these parameters that for the stream including a filter adsorber (GAC/sand), the segment apparent rate constants were higher near the top of the columns and indicated a sharper decrease with depth compared to the anthracite/sand first stage filters.

Results for chloral hydrate formation potential indicate very poor linearity in the first stage filtration and good linearity in the second stage filtration. This would indicate that CHFP removal could only be adequately modeled for a second stage filtration step. The AOXFP analysis indicated that some linearity existed for the first stage filtration and again better linearity was experienced for the second stage filtration. The earlier Edmonton study showed better linearity at the first stage filtration then the recent Edmonton study. This difference could be partially attributed to the use of air scour used during backwash for the recent Edmonton study, hence removing the biofilm and reducing AOXFP removal. It was noted that the AOXFP linearity was not improved for the filter adsorber, showing that adsorption was not a factor in the removal of AOXFP. The apparent rate constants were similar regardless of media type. The THMFP results were very similar to the results found for AOXFP. It was noted that THMFP for the Laval study indicated very poor linearity. Although the role of temperature will be addressed in the Chapter 7.0, another possibility exists. For the Edmonton 1992-1993 study, the non-ozonated filter stream showed the poorest linearity. The Laval study employed its ozonation step after the first stage filtration, indicating that to model the THMFP removal may require an ozonation step be employed prior to the first stage filtration. Finally, the chlorine demand results were very similar to the AOXFP results, also showing improved linearity at the second stage filtration. Again better linearity at the first stage filtration was found for the earlier Edmonton study, which could be due to the air scour step during backwashing for the most recent Edmonton study.

6.3 Ozonation by-products

The results included in this class of compounds were aldehydes and oxo-acids. The results for these two compounds showed the most variability among studies and among parameters. The best results were obtained for formaldehyde. This aldehyde showed the best linearity in the first stage filtration, and the chlorinated and non-ozonated stream produced the poorest linearity at the first stage filtration. The formaldehyde apparent rate constants were shown to be non-linearly related to EBCT when correlations were statistically significant . It was found that the highest apparent rate constants corresponded to the GAC/sand filters, however the Southern California study showed good removal for spent GAC filters, indicating that biological removal was the dominant removal mechanism, and adsorption would be secondary. For methyl glyoxal, results among four studies ranged from extremely poor (Edmonton 1992-1993) to excellent linearity (Cincinnati, Ohio). The apparent rate constants were not necessarily dependent on hydraulic loading rate, and were found to be more dependent on the filter media. The Southern California study showed poor linearity for the spent GAC filters which may suggest that adsorption was the dominant removal process. It was felt that the variability among these studies was attributable to differences in experimental protocol in addition to operating conditions.

It has been documented that aldehyde compounds are produced during a treatment process in the presence of an oxidant. The formation of these compounds can lead to odour problems (Hrudey et al, 1988a, Hrudey et al, 1988b, and Bruchet et al, 1992). The major assumption for this modeling method used in this thesis is that the parameter measured is being removed by the biological filtration process. Because some aldehydes are metabolic by-products of bacteria, it is reasonable to expect that there may be production of aldehydes during the filtration process, thereby reducing the removal rate or possibly even producing negative removal rates. This modeling method should be employed with caution when modeling aldehyde removals, since the formation of aldehydes in biological treatment processes has yet to be fully understood.

Results for glyoxal appeared to produce generally poor linearity for all studies, although it was noted that when some linearity was experienced the apparent rate constants were dependent on hydraulic loading rate. For acetaldehyde, the best linearity was observed in filters containing GAC. This would suggest that adsorption was the removal mechanism. For propanal, poor linearity was experienced in both first and second stage filtration, suggesting limited removal through biological and adsorption mechanisms.

The data available for oxoacids were the most limited for this research. It was observed that for all four compounds investigated, pyruvic acid, glyoxylic acid, ketomalonic acid and oxalacetic acid, linearity was poor for both first and second stage filtration. When some linearity was observed it was at the second stage filtration step. In general, rate constants for these compounds were independent of hydraulic loading rate. Since these compound were very limited in their applicability to the empirical modeling approach proposed, the oxoacids will not be discussed further.

6.4 Comparison among the classes of compounds

Although there were similarities noted among all parameters analyzed, there were several distinctions noted between each class of compound. The BOM parameters indicated a non-linear relationship between apparent rate constant and EBCT, except for the first stage filtration step for NVOC. The BOM parameters tended to show lower x-intercepts for higher EBCTs; however, the water temperature and influent concentration were influencing factors. For the chlorinated by-product precursors, all parameters showed a definite relationship between apparent rate constant and EBCT as seen with the AOC parameter. For the chlorinated by-product precursor parameters showing some first stage filtration linearity, the x-intercept was found to decrease with EBCT. The ozonated by-products displayed a distinct non-linear relationship for apparent rate constants and EBCT for formaldehyde only. It was noted that biological removal was suspected to be the dominant removal mechanism for formaldehyde, and that formaldehyde removal was predominantly achieved in the first stage filtration. Although varying results were obtained for other aldehyde compounds, it was demonstrated that adsorption could be the dominant removal mechanism. Oxoacids were found to be poorly modeled using this empirical method.

In general it can be said that filters operated using chlorinated water or without prior ozonation produce poor linearity for most of the parameters investigated. This observation was expected since ozonation has been shown to enhance the biodegradability of the substrate, improving its removal.

It was found that a distinct relationship existed between apparent rate constants and EBCT, and was seen in all classes of compounds. The apparent rate constant and EBCT nonlinear relationships were fitted to an equation in the form below:

$$x = ae^{-by}$$

The equations were intended to provide only a semi-quantitative basis for comparison. The equations were developed using only the Edmonton data in most cases. Occasionally, other study data was used when limited Edmonton data over a range of EBCTs existed (i.e. formaldehyde). An "a" and 'b" constant were selected for each curve through a trial and error process, and values for the constants were chosen when a curve was produced which best defined the data points, as determined by eye.

A Lack of Fit test was not performed on the curves, since fitting was done by eye, with only part of the available data. An equation was developed for AOC, DCAAFP, TCAAFP, chlorine demand, AOXFP, THMFP and formaldehyde.

These curves are shown on the same graph in Figures 88a and 88b. The "a" and "b" constants for each parameter measurement are summarized in Table 49. The results of the analysis identified three groups, representing different curve shapes.

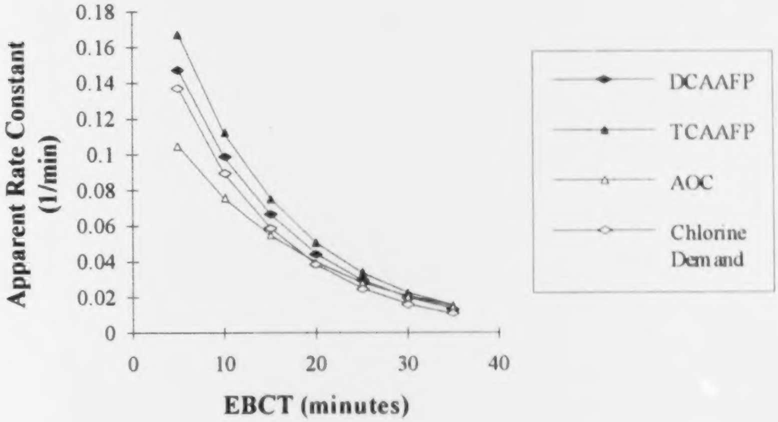


Figure 88a: Apparent Rate Constant versus EBCT for Analytical Measurements

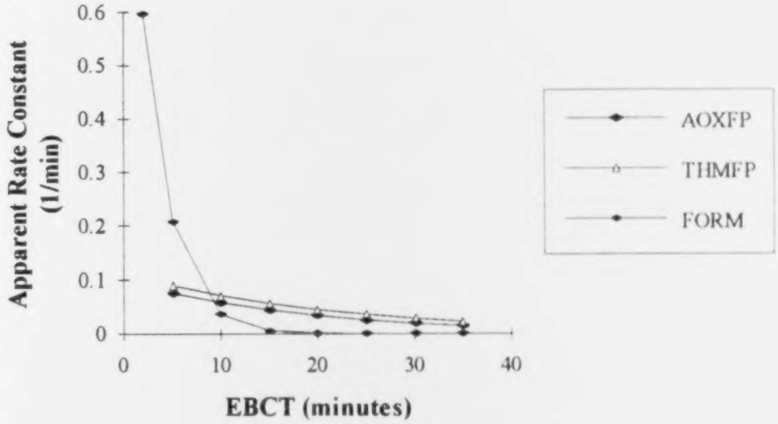


Figure 88b: Apparent Rate Constant versus EBCT for Analytical Measurements

Table 49

Summary of Constants for Curve $x = ae^{-by}$

Parameter	a	b
AOC	0.145	0.065
DCAAFP	0.220	0.080
TCAAFP	0.250	0.080
Chlorine Demand	0.210	0.085
AOXFP	0.100	0.055
THMFP	0.110	0.045
Formaldehyde	1.200	0.350

Similar curve shapes (i.e. a and b constants) were obtained for AOC, DCAAFP, TCAAFP and chlorine demand. Similar to this group but exhibiting a lower "a" and "b" constant was the group consisting of AOXFP and THMFP. The third group consisted only of formaldehyde. The equation for formaldehyde resulted in "a" and "b" constants of a larger magnitude than the other two groups identified.

The shape of the curves reflect the removal rate of the group of analytical measurements. Therefore the higher removal rate is apparent for formaldehyde, and the AOC, DCAAFP, TCAAFP and chlorine demand group is slightly higher than the AOXFP and THMFP group. This observation tends to agree with what is already known regarding these measurements. Aldehydes have been shown to be more readily removed due to the low molecular weight.

This observation would suggest that BOM and chlorinated by-product precursors other than for the haloacids would be the limiting parameters when modeling percent removal for all classes of compounds. These findings imply that a very useful and simple modeling technique is feasible for AOC, BDOC, HAAFP, AOXFP, THMFP, chlorine demand and formaldehyde. It is therefore suggested that an indicator compound from each class of compounds could be used to model removals for every compound within a specific class.

The exponential curve fit was found not to adequately fit all the apparent rate constants versus EBCT relationships. Therefore a more advanced curve fitting technique may be required to adequately fit the data.

The results presented above for Edmonton are based on apparent rate constants and x-intercepts that have been calculated for two separate filtration processes (first and second stage filtration). The influent to the second stage has therefore alreading had the most easily beodegradable material removed. It is noted that these calculations could be repeated using the total EBCT for the two filtration processes and therefore effectively represent only one filtration step (two filtration steps in series).

CHAPTER 7
THE ROLE OF TEMPERATURE

Temperature data were obtained for the Edmonton 1992-1993 study, the Cincinnati, Ohio study and the Laval, Quebec study. Table 55 summaries the temperature data for the period in which data was taken from three studies. Although this table is not complete, several important observations can be made. Obviously, the Cincinnati, Ohio study operated at a higher range of temperature than the Edmonton and Laval studies. Since a typical pretreatment has been observed to add approximately 3 to 4 °C to the finished water it is suspected that the raw water temperature for Cincinnati was approximately 16 ° C. The Laval study indicated the widest range of raw water temperatures, and it is suspected that the filter temperature ranged from 4 to 25 °C.

Table 50
Summary of Temperature Data

Study	Range of Filter Temperature, °C	Average Filter Temperature, °C	Range of Raw Water Temperature, °C
Edmonton 1992-93	5.1-12.6	9.25	2.5-9
Cincinnati, Ohio	13.9-27.5	20.18	n/a
Laval, Quebec	n/a	n/a	1-23

n/a -data not available

Only data for three parameters were obtained for the Cincinnati, Ohio study. These parameters were AOC-NOX, DCAAFP and methyl glyoxal. The AOC-NOX could not be compared to the Edmonton, and Laval study due to the difference in units and the absence of the Total AOC value. Despite these difference, the Cincinnati AOC-NOX data indicated very good linearity and apparent rate constants were found within the same range as the Edmonton and Laval studies. The Cincinnati DCAAFP results produced apparent rate constants in the same range as the Edmonton study for GAC/sand filters, however lower x-intercepts were achieved for the Cincinnati study. Although the influent DCAAFP concentration was higher for Edmonton, the higher water temperature experienced by Cincinnati could have contributed to the lower achievable removal concentration. In general, better linearity was observed in the Edmonton study; however, only a first stage filtration step was employed in the Edmonton Study. The methyl glyoxal data show the best linearity for the Cincinnati study. Since the Edmonton study indicated poor linearity for methyl glyoxal and little or no removal, it could be argued that perhaps higher temperatures are required to remove methyl glyoxal. There could be other reasons for the poor removal for the Edmonton study; however, the Southern California study was successful in removing methyl glyoxal and it is assumed that the warmer climate would lead to warmer water temperatures than Edmonton.

Comparing the results for Edmonton and Laval, it was observed that the TOC data produced similar rate constants for these studies; however, higher x-intercepts were obtained for the Laval study. It was noted that the influent TOC range was similar for both studies. Therefore, the cooler and more extreme temperatures experienced at the Laval plant may have attributed to the higher x-intercepts. This would indicate that during cooler temperatures the minimal achievable concentration would be higher than during warmer temperatures. A similar observation between the Edmonton and Laval studies was noted for the AOC and chlorine demand data. The AOC and chlorine demand data from these studies produce very similar apparent rate constants; however, the x-intercept values varied significantly. Although the AOC and chlorine demand influent concentration for Laval was higher than Edmonton, temperatures could have contributed to the higher x-intercepts.

It has been noted that the apparent rate constants may not be influenced by temperature; however, comparison of the results for THMFP contradicts this observation. THMFP for the Edmonton, and Laval studies was the only parameter common between these two studies which produced very different results. The THMFP apparent rate constants for Edmonton indicated very good linearity at the first and second stage filtration. The THMFP results for Laval indicated very poor linearity. Figures 89 and 90 show the THMFP relationship for the two Laval BAC contactors with the corresponding temperature for each data point.

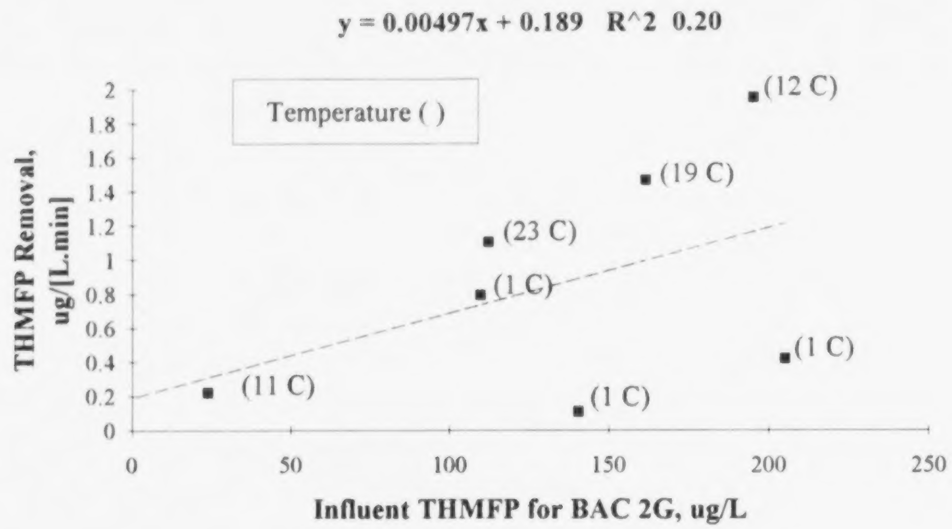


Figure 89: THMFP Removal Rate vs. Influent Concentration with Temperatures for BAC 2G, Laval, Quebec Study

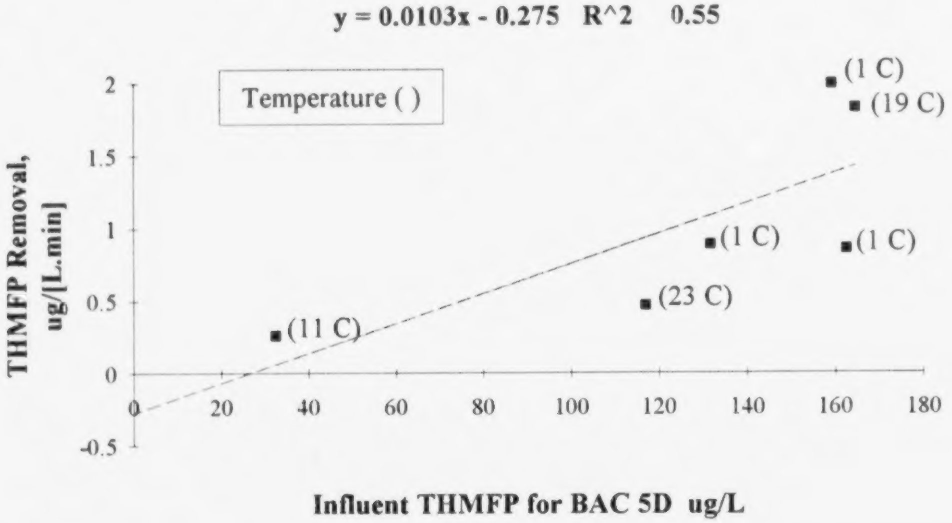


Figure 90: THMFP Removal Rate vs. Influent Concentration with Temperatures for BAC 5D, Laval, Quebec Study

It was thought that a quantitative temperature correction for the apparent rate constant could be attempted for the Laval, Quebec Study. Figures 89 and 90 indicate that the temperature does appear to affect the removal rate; however, there does not appear to be a proportional relationship indicating that other factors would influence the removal rate in addition to temperature. Therefore, it can only be said that the THMFP parameter would appear to be more temperature sensitive than other parameters, namely, AOC, TOC and chlorine demand. In addition it could be said that temperature appears to influence the minimum removal concentrations of these same parameters. A final observation might suggest that temperature may influence the removal of methyl glyoxal.

CHAPTER 8

APPLICATION TO WATER TREATMENT DESIGN

This section will demonstrate the usefulness of this research to design a biological water treatment filtration system to obtain desired removals for individual parameters. To illustrate the practical applications for the findings from the research, two examples will be worked through to interpret all of the conclusions. Although not illustrated in these examples, if a design calculation were to be performed to predict removal rates, a safety factor would need to be applied to the apparent rate constants and x-intercepts (S_{min}). One way of determining these safety factors would be by using the lower confidence bound for apparent rate constants and y-intercepts. The design calculation illustrated in this section should be regarded as providing a preliminary indication of the capability of biological treatment in a given situation. This would need to be confirmed by on site pilot testing.

EXAMPLE #1

For the purpose of the first example it will assumed that the biological filter design is intended for an Edmonton facility, and similar conditions to the Edmonton 1992-1993 study will be used since this study has provided the most data for this research. (It was noted in performing the analyses in this thesis that the minimum achievable concentration was water-specific, even though apparent rate constants were not. This matter is outside the scope of the present research, but should receive further study.) For this example, assume the following information is given; 1) The biological filters are to be designed to removal 80% of AOC, TCAAFP and formaldehyde (note that these parameters represent a different class of compound). 2) The range of raw water temperature is 3 to 10 °C, and 3) The following filter influent concentration ranges have been given for each compound;

AOC:	12 to 130 C eq μg acetate/L
TCAAFP:	11 to 140 μg/L
Formaldehyde:	0.5 to 65 μg/L

This analysis will determine the EBCT, type of media and number of filtration stages to meet the above criteria. In addition the limiting parameter will be identified and the most cost effective option will be recommended.

AOC

To design a filtration system to removal 80% of AOC, Figure 29, displaying the apparent rate constants versus EBCT was first referenced. This figure illustrates that there is no advantage to operate at EBCTs greater than 30 minutes, since the shape of the curve tends to flatten out at this point indicating limited additional AOC removal beyond this point. This curve also indicated than there is removal beyond a typical first stage filtration step, suggesting the a second stage filtration may be an option in this case.

This first filtration stage will consider first a high hydraulic loading rate and next a low hydraulic loading rate to evaluate which rate would achieve the highest removal. It has been shown that the best linearity corresponds to pre-ozonated streams. Therefore non-ozonated and chlorinated streams will not be considered. From Figure 29 and Table 13 and 14, a high hydraulic loading rate (short EBCT) for an ozonated stream gives an apparent rate constant of 0.125 min^{-1} for an EBCT of 4.5 minutes, and 0.080 $min\text{-}^{1}$ for an EBCT of 11.0 minutes. The corresponding x-intercept for 4.5 minutes is 15 μg/L, and for 11.0 minutes is 16 μg/L. There appeared to be little difference between anthracite and GAC filters. It should be noted that emphasis should be placed on choosing the x-intercept for an influent concentration range and water temperature from a study similar to the design specifications.

Using the above information the following graph (Figure 91) can be generated. In addition to the actual linear relationship generated, individual graphs for Edmonton studies were viewed to determine the minimum influent AOC concentration. This was completed to estimate an minimum achievable concentration which was higher than the x-intercept value since the biofilm model suggests that the actual S_{min} value would intersect the x-axis showing a curved relationship. This is illustrated in Figure 91. This design x-intercept is a more conservative value and could be referred to as a safety factor. Ideally a safety factor could be applied to x-intercepts when factors such as temperature are unknown.

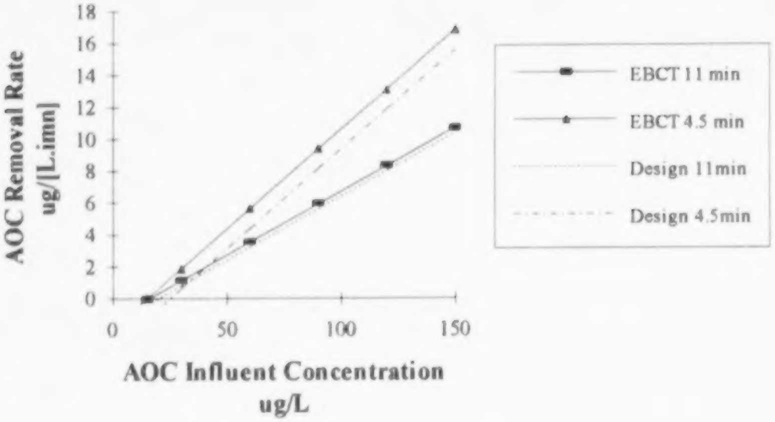


Figure 91: Predicted AOC Removal Rate vs. Design Influent Concentration for two different EBCTs

From the information provided in Figure 91, a percent AOC removal vs. influent concentration relationship can be generated for the two EBCTs. This relationship can be seen in Figure 92. This graph indicates that for a first stage filtration, only the longer EBCT provides the most removal; however, neither design EBCTs can remove the required 80% AOC. This would indicate that a second filtration stage would be required.

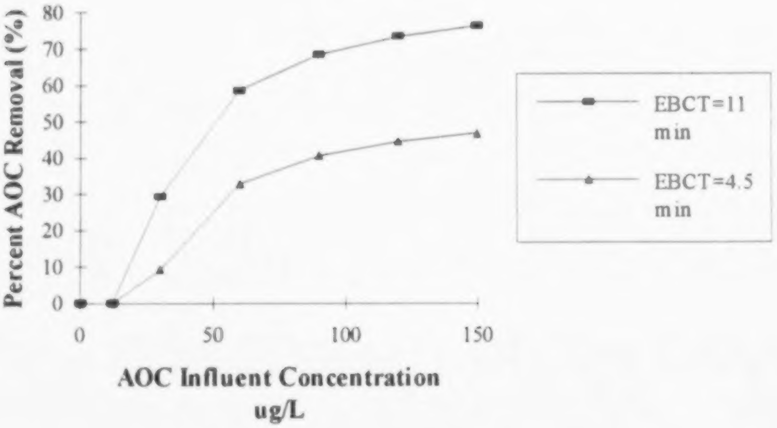


Figure 92: Percent AOC Removal vs. AOC Influent Concentration for first stage filtration

Apparent rate constants for two EBCTs for GAC contactors from the Edmonton studies were chosen. For an EBCT of 19 minutes an apparent rate constant of 0.046 min^{-1} was used, and for an EBCT of 36 minutes, an apparent rate constant of 0.022 $\text{min}^{-1}$was used. The 19 minute EBCT indicated a negative x-intercept. Inspection of the actual graphs revealed that 10 μg/L was a reasonable x-intercept. The x-intercept for the 36 minute EBCT indicated an x-intercept of 5.5, however a value of 8.0 μg/L was used in the analysis. Figure 93 displays the percent AOC removal for the second stage filtration. The effluent from the first stage filtration was used as the influent for the second stage filtration. This relationship indicates that when influent concentration are greater than 60 μg/L, 75% removal can be maintained.

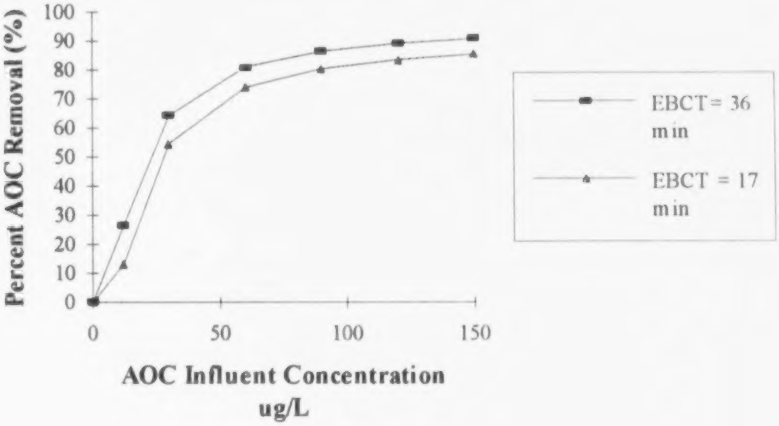


Figure 93: Percent AOC Removal vs. AOC Influent Concentration for Second Stage Filtration

TCAAFP

The analysis for TCAAFP was completed in the same manner as for AOC. First Figure 45 was viewed. This figure shows that TCAAFP can still be removed at second stage filtration or at the 30 minutes EBCT. From Figure 45, a high hydraulic loading rate (short EBCT) for an ozonated stream gave an apparent rate constant of 0.120 min^{-1} for an EBCT of 5.5 minutes and 0.065 min-^{1} for an EBCT of 11.0 minutes. The corresponding x-intercept for 5.5 minutes was 25.6 μg/L, and for 11.0 minutes was 4.3 μg/L. The filter adsorber (Filter 4) appeared to show higher removal than the anthracite filters. To be conservative, higher x-intercepts were chosen for the analysis. An x-intercept of 26 µg/L for the 5.5 minute EBCT indicated a reasonable value when viewing the original graphs. The 11 minute EBCT used an x-intercept of 9.0 µg/L. Figure 94 displays the calculated TCAAFP removal rates versus influent concentration in addition to the design relationships. It was noted in Figure 94 that the lines crossed, since the x-intercept for the 5.5 minute EBCT was almost three times the x-intercept for the 11 minute EBCT.

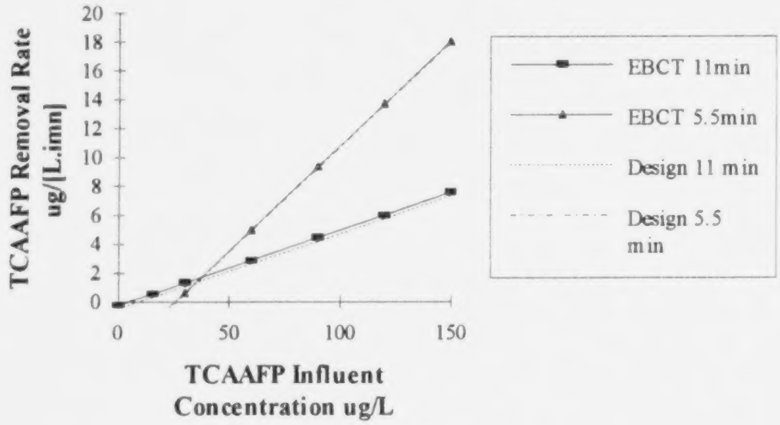


Figure 94: Predicted TCAAFP Removal Rate vs. Design Influent Concentration for two different EBCTs

From this information a percent TCAAFP removal versus influent concentration was completed (Figure 95). Figure 95 indicates that the higher EBCT filter would produce the higher removal, as expected. The shorter EBCT filter can remove only 50% of the influent TCAAFP at the first stage filtration and would require a second stage filtration.

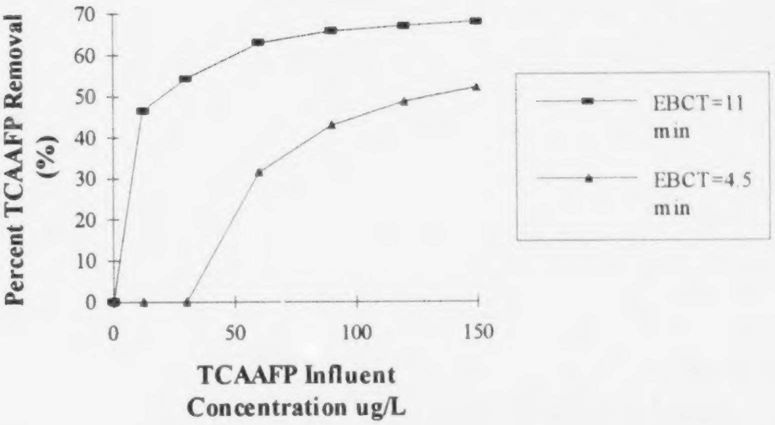


Figure 95: Percent TCAAFP Removal vs. TCAAFP Influent Concentration for first stage filtration

Apparent rate constants for two EBCTs for GAC contactors from the Edmonton studies were chosen. For an EBCT of 17 minutes an apparent rate constants of 0.042 min^{-1} was used, and for an EBCT of 34 an apparent rate constant of 0.024 $\text{min}^{-1}$was used. The 17 minute EBCT indicated a low x-intercept. Inspection of the actual graphs revealed that 7.5 μg/L was a reasonable x-intercept. The x-intercept for the 34 minute EBCT indicated an x-intercept of 4.9 μg/L and inspection of the original graphs indicate that this was a reasonable value. Figure 96 displays the percent TCAAFP removal for the second stage filtration. This relationship indicates that when influent concentrations are greater than 50 μg/L, 75% removal could be maintained in the filter with EBCT of 36 minutes, and concentrations greater than 100 μg/L could be maintained at 80% removal in the 17 minute EBCT filter. It should be noted that this calculation assumes that the nature of the substrate remained the same when the substrate concentration increases.

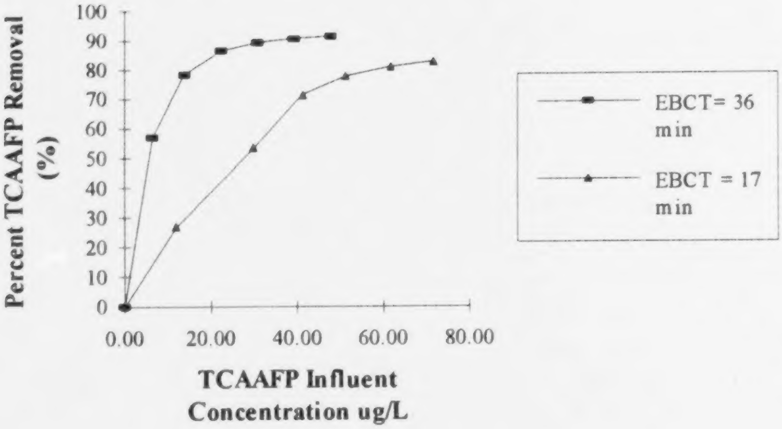


Figure 96: Percent TCAAFP Removal vs. TCAAFP Influent Concentration for Second Stage Filtration

Formaldehyde

The analysis for formaldehyde was completed by first viewing Figure 77. This figure indicates that there in little advantage in operating filters beyond 15 minute EBCTs. From Table 36, a high hydraulic loading rate (short EBCT) for an ozonated stream gave an apparent rate constant of 0.095 min^{-1} for an EBCT of 5.5 minutes and 0.072 min-^{1} for an EBCT of 11.0 minutes. The corresponding x-intercept for 5.5 minutes was 5.2 μg/L, and for 11.0 minutes was 3.2 μg/L The filter adsorber (Filter 4) and the anthracite filters appears to also have similar apparent rate constants and x-intercepts for the same EBCTs. The x-intercepts were determined to be reasonable when viewing the original graphs. Figure 97 displays the percent formaldehyde removal rate versus influent concentration. This figure indicates that for the higher EBCT a 70% removal could be maintained for influent concentrations greater than. 25 μg/L. Although the second stage filtration is not shown here, it would be safe to say that an additional 10% of the influent could be achieved at that stage.

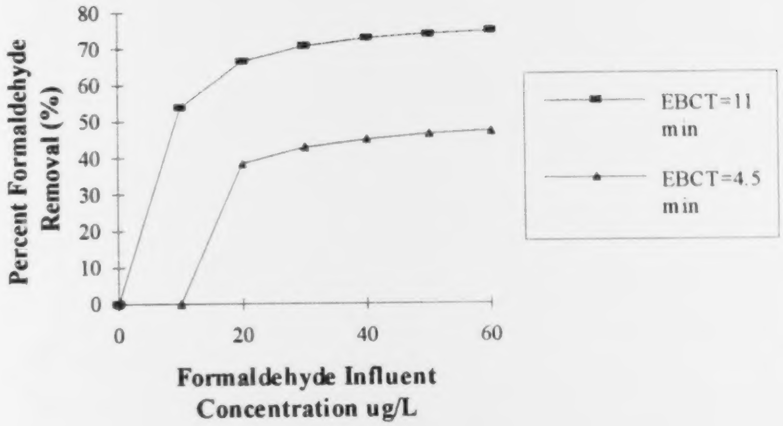


Figure 97: Percent Formaldehyde Removal vs. Formaldehyde Influent Concentration for first Stage Filtration

The results of this analysis shows that the AOC and TCAAFP would be the limiting parameters and therefore require a second stage filtration to achieve an 80% removal for a high percent of the operating time. It would be recommended in this case to operate a preozonation step prior to filtration. The first stage filtration could be either an anthracite or GAC sand filter since the performance for these two filters were similar for these three parameters. The first stage filtration is recommended to be operated at an EBCT of 11 minutes. The second stage filtration is recommended to be a GAC contactor and operated at a minimum EBCT of 30 minutes.

EXAMPLE #2

A second example will demonstrate a method to estimate a required operating EBCT to achieve a specific effluent concentration for AOC, TCAAFP and formaldehyde. Initially several EBCTs were selected. The apparent rate constants versus EBCT and minimum achievable concentration versus EBCT graphs were used to formulate a removal rate equation for AOC, TCAAFP and Formaldehyde for each EBCT. Using several possible criteria for effluent concentrations for AOC, TCAAFP and formaldehyde, a permissible influent concentration was calculated for each EBCT.

For AOC, Figure 98 was developed using three criteria for AOC effluent concentrations. Using the range of influent concentrations for the Edmonton study (12 to 130 C eq μg acetate/L), Figure 98 indicates that an EBCT of 35 minutes is required to meet the effluent concentration of 20 μg/L. Target concentrations less than 20 μg/L could not be consistently achieved at any EBCT.

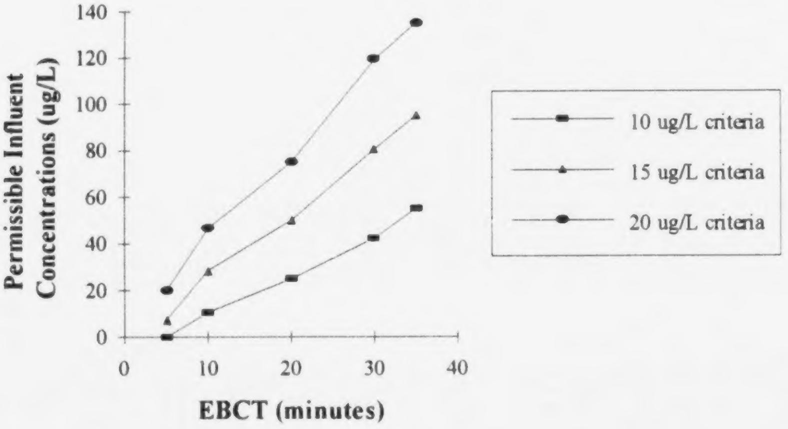


Figure 98: Permissible Influent Concentrations versus EBCT for AOC

For TCAAFP, Figure 99 was developed using three criteria for TCAAFP effluent concentrations. Using the range of influent concentrations during the Edmonton study (11 to 140 μg/L), Figure 99 indicates that an EBCT of 15 minutes could meet the criterion if the concentration was 30 μg/L. An EBCT of 30 minutes could meet a criterion of 20 μ g/L. If the criterion was 10 μg/L, no EBCT would be suitable for the range of Edmonton influents.

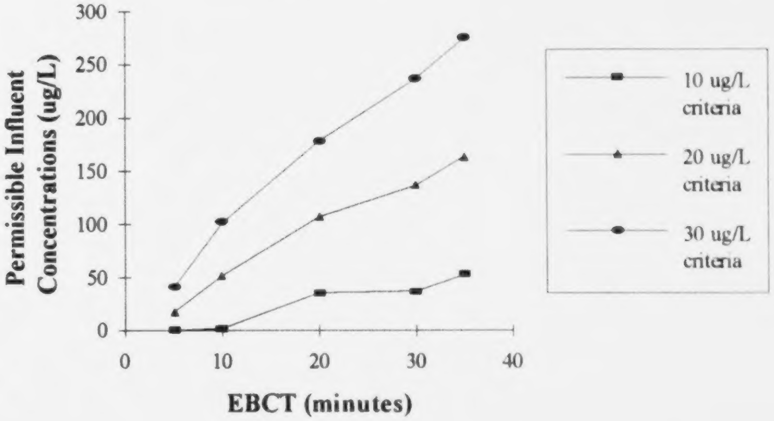


Figure 99: Permissible Influent Concentrations versus EBCT for TCAAFP

For formaldehyde Figure 100 was developed using three criteria for formaldehyde effluent concentrations. Using the range of influent concentrations during the Edmonton study (0.5 to 65 μg/L), Figure 100 indicates that an EBCT of 5 minutes could meet the criteria if the concentration was 15 μg/L. An EBCT of 30 minutes could meet the criteria if the concentration was 10 μg/L. If the concentration criteria was 5 μg/L, no EBCT could consistently meet it for the range of Edmonton influents.

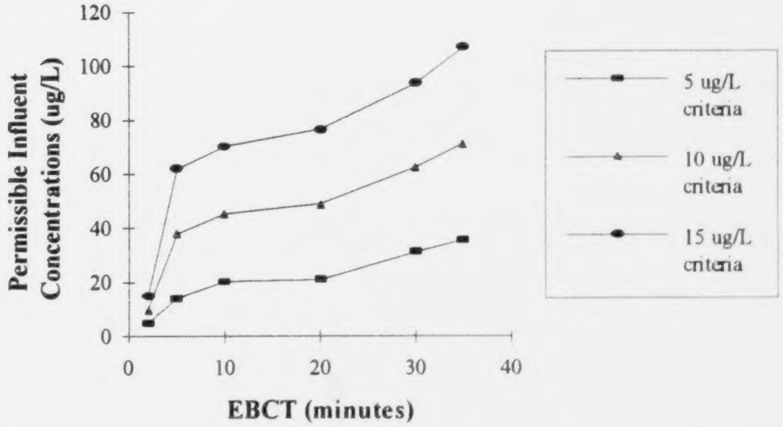


Figure 100: Permissible Influent Concentrations versus EBCT for Formaldehyde

Assume that the effluent concentration criteria for an Edmonton study were 20 μg/L for AOC, 30 μg/L for TCAAFP and 10 μg/L for formaldehyde. For this example the AOC would be the limiting parameter requiring the filtration process to operate at an EBCT of 35 minutes. The limiting parameter could vary according to seasonal conditions. In this case it may be possible to operate the system at lower EBCTs and subsequently increase the EBCT during spring runoff. To achieve a lower EBCT operationally, a lower hydraulic loading rate could be employed.

CHAPTER 9

Conclusions and Recommendations

9.1 Conclusions

There are several important conclusions and recommendations as a results of this research. They are outlined below.

1. An empirical first order modeling approach was found to be useful to describe the removal of BOM, chlorinated by-product precursors and ozonated by-products during biological treatment. The modeling was based on plotting the apparent rate constant, k (based on EBCT) versus the influent concentration to the filter or BAC contactor. Table 51 lists the parameters showing good linearity at the first and second stage filtration. For BOM parameters, good linearity was observed in all parameters investigated (NVOC, AOC and BDOC) for both a first and second stage biological filtration. For chlorinated by product precursors, good linearity was observed in first and second stage filtration for DCAAFP, TCAAFP, AOXFP, and THMFP. Good linearity for chloral hydrate formation potential and chlorine demand was found for the second stage filtration only. For ozonated by-products, formaldehyde was the only aldehyde to consistently display good linearity. Other ozonated by-products showed some linearity, however adsorption was suspected to be the dominant removal mechanism.

Table 51

Summary of Parameters Showing Good Linearity at First and Second Stage Filtration

BOM	Chlorinated By-Products	Ozonated By-Products
NVOC	DCAAFP, TCAAFP	Formaldehyde
AOC	AOXFP, THMFP	
BDOC	Chorine Demand *	
	Chloral Hydrate *	

* good linearity observed at the second stage filtration only

2. In general, filters which were ozonated prior to filtration, and were not chlorinated or backwashed with chlorinated water, produced statistically significant linear correlations between apparent rate constants and influent concentration.

3. A non-linear relationship was found between apparent rate constants and EBCTs for AOC, DCAAFP, TCAAFP, AOXFP, chlorine demand, THMFP and formaldehyde. In all cases the apparent rate constant decreased approximately exponentially with time, indicating that each of those parameters represent a suite of compounds of different biodegradability. It should be noted that the second stage apparent rate constants received a prior first stage removal, therefore started with a less biodegradable substrate.

4. The relationship described in conclusion 3 was obtained by pooling the rate constants from various studies. This observation suggested that apparent rate constants were similar between studies despite differences in water sources and operating conditions.

5. The x-intercept, which represented the minimum achievable concentration, varied significantly between studies, although a nonlinear relationship between the x-intercepts and EBCTs was observed for some parameters. This parameter was found to depend on influent concentration and operating temperature.

6. For the parameters discussed in Conclusion 3, a curve was developed to describe qualitatively the relationship between apparent rate constants and EBCT. Using these curves, and the x-intercept (S_{min}) and EBCT, predictions for a given percent removal were made for a known range of influent concentrations. Further to this, an equation for a range of EBCTs could be developed using the apparent rate constant versus EBCT and x-intercept and EBCT relationships. Using a desired effluent concentration criteria, a maximum permissible influent concentration could be determined. In addition, using a known effluent concentration criterion and a range of influent concentrations, an EBCT was calculated to meet the design criteria. Thus this research has led to the development of a simple, practical relationship for preliminary design of biological contactors for drinking water treatment. The modeling technique also demonstrated how a safety factor could be applied to x-intercepts to provide a conservative design when parameters such as temperature and range of influent concentrations are unknown.

7. The data suggested that temperature may influence the removal of THMFP and methyl glyoxal more than other parameters investigated.

8. It was observed that particularly with aldehyde compounds, the removal was sensitive to the length of time the filters were operational. Therefore, it may be required that a filter be operated longer to achieve consistent removal rates for some aldehyde compounds.

9.2 Recommendations

1. It is recommended that the phase II experiments for the Edmonton study, which are to commence at the conclusion of this research, should operate the first stage filter using no air scouring step during backwashing. It is hoped that discontinuing the air scour will provide more consistent removals leading to better linearity in the apparent rate constant versus influent concentration relationship.

2. It is not recommended that aldehydes be used as a surrogate for AOC analysis, as has been proposed by Krasner et al (1992). The non-linear relationship for apparent rate constant versus EBCT for aldehydes indicated that the majority of these compounds were removed at short EBCTs, which corresponded to the first stage filtration. AOC removal was achieved at both first and second stage filtration, therefore it is the limiting parameter of the two. If aldehydes were used as a surrogate analysis for AOC, it would overestimate the removal of AOC.

3. This modeling technique could only apply to filters and GAC contactors operating at relatively steady EBCTs. It was demonstrated that since the apparent rate constants are non-linearly related to EBCT, the EBCT must remain constant to produce a linearly significant apparent rate constant and represent near steady state conditions. In addition, the biofilm may be non-steady-state if EBCT is changing.

4. The results presented here can offer a relatively simple method for predicting removal rates, percent removal, or design EBCT to meet effluent concentration criteria for many parameters. It is recommended that additional experiments using different water sources be conducted. These experiments should use similar operating conditions (i.e. same ozonation step, media type). These could be run for long periods of time and each stream should be operated at a different EBCT. The results would produce many

points and it would be hoped that apparent rate constant versus EBCT and x-intercept versus EBCT relationships would be clearly defined. Should good non-linear relationships be obtained, an advanced curve fitting technique could be employed to better fit the non linear relationship. Finally, equations for a range of EBCTs could be developed and used to predict design EBCTs to meet effluent concentration criteria. EBCTs could then be predicted using equations and the actual measurements could test their validity.

5. It is recommended that the empirical modeling method could also provide the framework for a more advanced modeling application.

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APPENDIX A

Introduction

This section describes the design, construction and operation of a drinking water treatment pilot plant in Edmonton, Alberta that has been used for several biological drinking water studies. This section focuses on the original design objectives for the pilot plant, with emphases placed on the refurbishment activities, completed to adapted the pilot plant for a biological water treatment study designed for organic control.

The pilot plant initially employed a conventional drinking water treatment design involving coagulation, flocculation and sedimentation. In the phase I design, water was stored in a settled water storage tank and then split into three streams which applied an oxidation step. One stream received no treatment and was subsequently followed by dual media and GAC filtration. The second stream was chlorinated prior to dual media filtration only. The third stream was ozonated and subsequently divided into three more streams and was followed by dual media and GAC filtration. Figure A-1 provides a schematic diagram for the pilot plant during phase I experiments. All material used to construct this pilot plant were organically inert (stainless steel, Teflon®, glass or a fluorocarbon). The following sections will provide a detailed description of all components employed in this pilot plant which has been adapted after Milne et al, 1990.

Raw Water Supply

The pilot plant was located at the Rossdale water treatment plant in Edmonton, Alberta. The Rossdale water treatment plant is located in the city's centre along the North Sackatchewan river. The pilot plant was located on the fourth floor of the Recal building and was enclosed in a 5 m x 10 m room constructed of lumber and drywall. A positive pressure was maintained and a filtered air system was provided to minimize dust in the air. All doors to the room were sealed and, and two vents were provided. One was located on the north-west wall, and the second was located in the ceiling where the top of both ozone contactors penetrate the main vent for the Recal Building. Figure A-2 provides a plan view of the pilot plant.

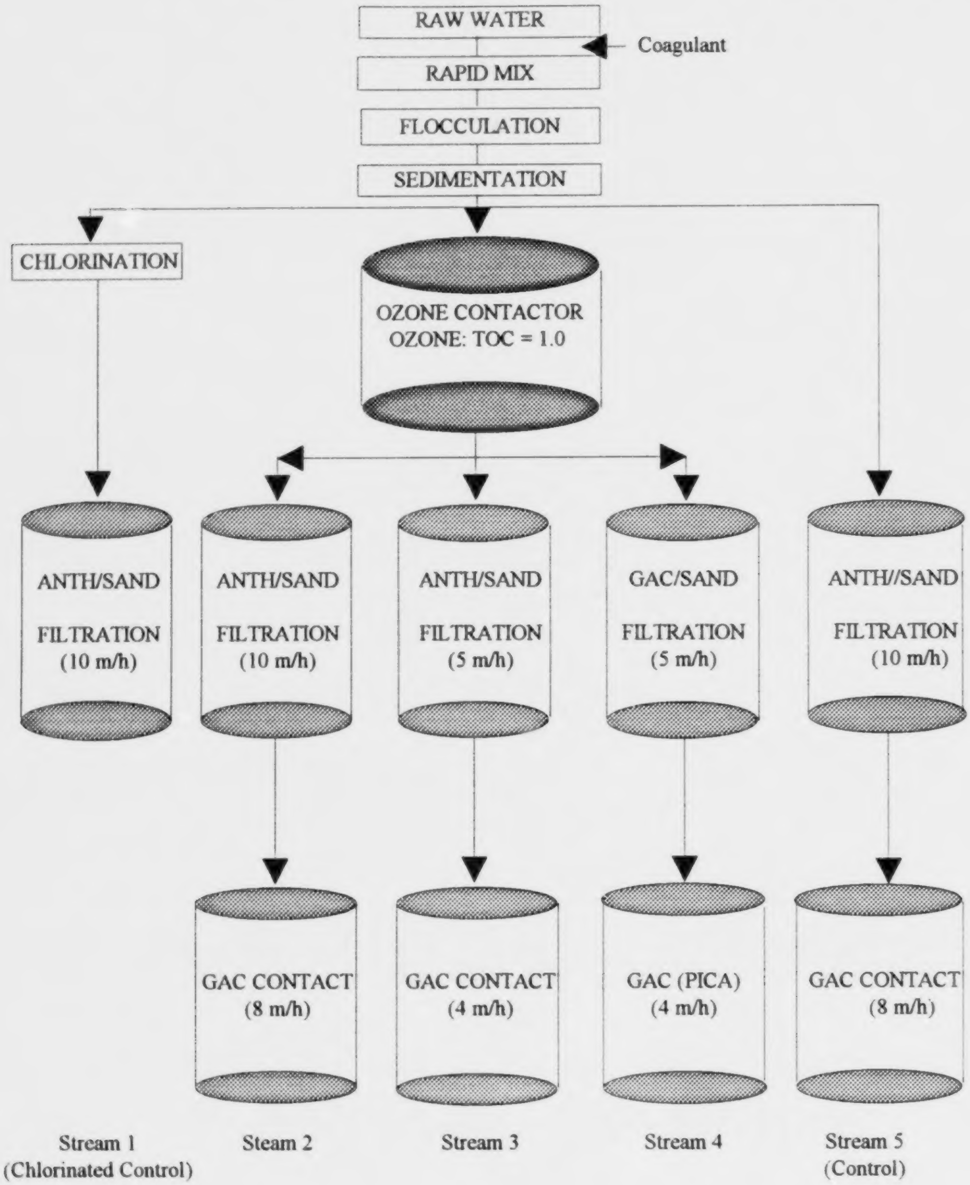


Figure A1: Schematic for the Edmonton, Alberta Pilot Plant 1992-1993 (Phase I)

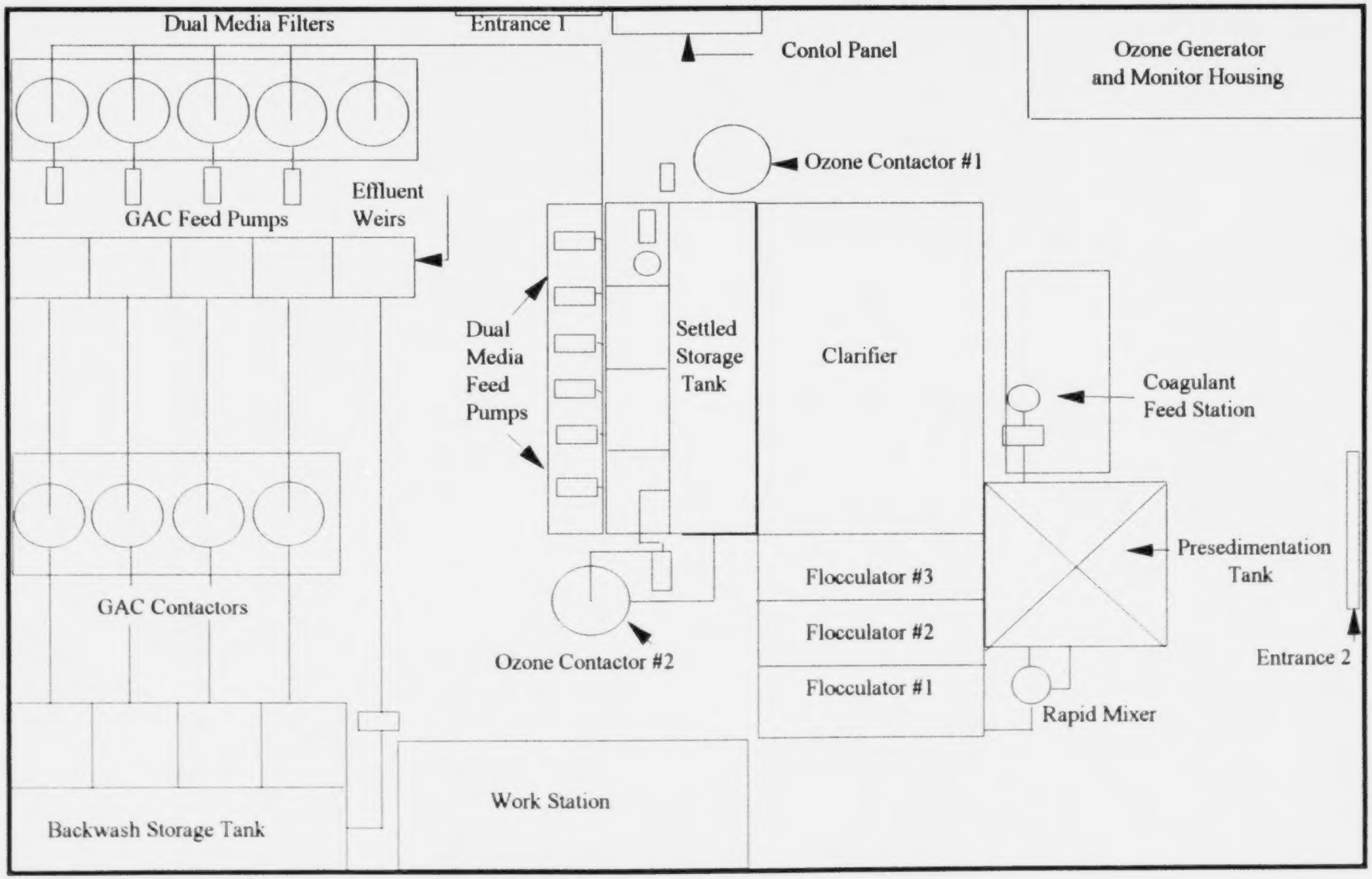


Figure A-2: Plan View of the Edmonton, Alberta Pilot Plant

Water from the river was pumped to three plants at the Rossdale location, and raw water from plant three was pumped to the pilot plant through a centrifugal booster pump. A screen with a 3 mm size opening was provided to remove large particles. This screen was automatically backwashed every 40 minutes to prevent the screen from clogging.

A problem with fluctuating raw water inflow was encountered in previous studies, and was recognized as a potential problem in this study. The raw water inflow was controlled by the pressure in the plant three intake line, and typically the pressure decreased overnight and increased in the morning, afternoon and evening. This pressure fluctuation often caused dangerously low water levels in the settled water storage tank which could lead to air locks in the pumps feeding the filters. To alleviate this problem, a pressure sensing valve was installed in the raw water line and connected to a pressure control device to allow a constant pressure to be maintained in the intake line.

The intake pump was located on the first floor of the Recal building, and was pumped to the fourth floor where the pilot plant was located. The average incoming flowrate was 40 L/min. This flowrate had been observed to vary by only five percent.

Pre-sedimentation

A pre-sedimentation tank was located at the north side of the pilot plant room (Figure A-2). The function of this tank was to minimize the loading of very high suspended solids which accompany spring runoff in the North Saskatchewan river. The design of the tank was such to remove silica particles greater than 0.05 mm. The tank was cone shaped, and had a residence time of 9.3 minutes and overflow rate of 4.15 cm/min. A blowdown flow rate of approximately 10 L/min was maintained at the base of the tank . Other specific dimensions are found in Table A-1.

Table A-1
Pre-sedimentation Tank Design Specifications

Parameter	Value
Height	300 mm
Cone Height	650 mm
Width	850 mm
Depth	850 mm
Volume	373.3 L
Flowrate	30 L/min
Blowdown rate	10 L/min
Overflow area	0.7225 m^2
Overflow rate	4.15 cm/min
Residence Time	9.3 min
Design Sediment Removal	> 0.05 mm

Coagulation

Coagulation was achieved through the raw water with a high intensity, low detention time rapid mixer. The design utilized an open, baffled, cylindrical tank with a detention time of 17 seconds. Water entered the bottom of the mixer and overflowed the top. The coagulant was injected at the base of the mixer. As a result of a series of jar tests, the coagulant chosen was Aluminex I®. This coagulant was used independent of organic polymer. The coagulant dosage varied seasonally from 20 to 120 mg/L. The coagulant was feed undiluted using a Cole Parmer Master Flex® chemical feed pump. Mixing was accomplished with a variable speed (0-3600 rpm) agitator with two closely spaced impeller blades, of opposite pitch, mounted on a common vertical shaft. The design specification for the coagulation treatment step are provided below in Table A-2.

Table A-2
Coagulation Design Specifications

Parameter	Value
Coagulant Dosage	20-120 mg/L
Rapid Mix :	
Height	500 mm
Diameter	154 mm
Baffle Height	50 mm
Baffle Width	67 mm
Residence Time	17 s
Blade Length	75 mm
Blade pitch	30 °
Speed	1100 rpm
Flow rate	30 L/min
Volume	9.31 L

Flocculation

A three stage tapered flocculation was utilized. The flocculation compartments were divided by baffles, and each had a 60° tapered bottom for sludge withdrawal, and manually adjusted valves to control blowdown rate. Each compartment was equipped with a horizontal, axial-flow turbine flocculator, driven by a variable speed (0-3600 rpm) drive motor with a 1:17 reduction gearbox. The individual flocculators consisted of four-blade, oppositely pitched turbine type impellers, spaced uniformly across the width of the tank. The bearings were blocks of Teflon® bolted to the side walls of the compartments to which the drive shafts penetrated. These required frequent replacement, since they deformed over time by the horizontal shafts. A slight leakage was experienced from these Teflon® bearing (approximately 1 L/min) and leakage was collected on the outside wall and run to waste.

The flocculators were operated in a decreased velocity gradient from 40, 20 to 12 rpm. During periods of operation when high turbidity and colour were experienced, excellent flocculation was achieved. During periods when low turbidity and colour were experienced, smaller flocs were developed and a thin scum formed on the surface of the clarifier. The scum was vacuumed off every two days to prevent Aluminex floc from leaving the clarifier. The blowdown valves were always kept closed during operation, and opened only during monthly cleaning of the sedimentation tank. Flocculation design specifications are provide in Table A-3.

Table A-3
Flocculation Design Specifications

Parameter	Valve
Reduction gearbox	1:17
Velocity gradient	40, 20, 12 rpm
Height	850 mm
Width	1250 mm
Length	300 mm
Freeboard	110 mm
Slant angle	60 °
Slant height	260 mm
Tank Volumes	367.5 L
Detention Time (three stage)	37 min
Flow rate	30 L/min

Sedimentation

The flocculated water entered the clarifier through a perforated baffle. The performance of the clarifier was further improved with the addition of 60° parallel plate settlers, spaced at 50 mm internals, and occupying about 60 percent of the Clarifier surface area. Sludge removal was designed to provide the removal of sludge on a continual basis by means of a perforated pipe running across the bottom of the inlet end of the tank. Unfortunately, this sludge removal system was not very effective. The slope of the clarifier tank was not adequate to provide an effective gravity removal, and by increasing flowrates from the base of the tank did not aid the removal process. To compensate for this problem the clarifier was drained and cleaned once a month and more frequently during spring runoff. During periods where low raw water turbidity and colour existed, a scum layer was formed on the surface of the clarifier in addition to the surfaces of flocculators 2 and 3. This was a result of the formation of small and light flocs, during these conditions. Experiments using a polymer were found to improve this problem, however concern with the possible sensitivity of the biofilm to the polymer was recognized. Therefore, the scum layer was removed using a vacuum every other day to compensate for this problem.

The clarifier effluent entered three submerged orifice launders near the outlet end of the tank and discharged by gravity into the settled water storage tank. These perforated orifices prevented the discharged of some floating material from the clarifier to the downstream processes. Clarifier design specifications are provided in Table A-4.

Table A-4
Clarifier Design Specifications

Parameter	Value
Height	850 mm
Angle Height	400 mm
Depth	1250 mm
Length	1750 mm
Surface area	2.1875 mm^2
Volume	2078.3 L
Freeboard	100 mm
Plate separation	50 mm
Plate angle	60 °
Flow Rate	18 L/min
Blowdown rate	12 L/min
sludge withdrawal angle	12.9 °
residence time	69.8 min
overflow rate	0.82 cm/min
launder type	submerged effluent

Settled Water Storage Tank

The settled water storage tank served as : 1) a hydraulic buffer, to prevent interruption of flow to downstream processes during clarification; 2) a split box, from which the flow was divided into three different pre-oxidation streams in phase I; and 3) a constant head tank. The detention time was approximately 15 minutes. An overflow outlet was provided to allow a constant head in the tank, and gravity flow resulted in the discharge to the pre-oxidation streams.

Pre-oxidation Step

The phase I pre-oxidation streams included a non-oxidation stream (5), a chlorinated stream (1) and an ozonated stream, which was subsequently divided into three more streams (2, 3, and 4).

Control Stream (no-oxidant)

The control stream (5) was designed with no oxidation step prior to dual media filtration. Water from the settled water storage tank was diverted to a separate (buffer) tank by gravity. The separated tank held 126.4 L of water and provided a constant head of 320 mm. The water was allowed to flow from a small pipe (½ inch) at the base of the tank to a March centrifugal pump.

Chlorinated Stream

The chlorinated stream (1) was designed to provide a non-biological stream and also represent a conventional pre-chlorinated step prior to dual media filtration. Water was diverted to a separate (disinfection) tank by gravity. The dimensions of this tank were the same as the control stream tank. At the effluent location of the settled water storage tank, a chlorine solution was fed by a chemical feed pump at a rate to provide a free chlorine residual of 0.5 mg/L prior to filtration. The chlorine solution was obtained using a 4 percent solution of sodium hypochlorite at a 1:5 dilution with de ionized water. The chlorine solution was stored in a dark glass container to prevent light exposure and fed at a rate of approximately 1.0 mL/min. The residence time of this disinfection tank was 28 min. The chlorinated water was allowed to exit a small pipe (½ inch) at the base of the tank to a March centrifugal pump.

Ozonation

In phase I, water for the ozonation stream was withdrawn from the settled water storage tank and injected into the top of the ozone contactor at approximately 7 L/min. Ozone was passed through a porous glass diffuser at the bottom of the column and the system was operated in a counter-current mode. The ozone contactor where constructed of stainless steel, having an inner diameter of 225 mm and was approximately 3 m in height. These dimensions provided for a detention time of 16.3 min. The ozone contactor consisted of a 2 m cylinder which was joined with an additional 1 m cylinder, adapted for this study to provide a second ozone contact stage. All extensions were joined using Teflon® gaskets. The diffuser was sandwiched between two stainless steel rings and sealed through the use of Teflon® o-rings. This diffuser provided bubbles with a size range of 2-4 mm and provided an even dispersion of gas throughout the cross-section of the contactor. Ozonated water exited the bottom of the contactor and flowed by gravity to a dissipation tank. The flow was controlled by a globe valve to provide a constant head in the ozone contactor. An overflow line was attached at the design head level (2.86 m) of the contactor and a small overflow was allowed to ensure a constant head would be maintained. The dissipation tank was designed to allow for dissipation of the ozone residual prior to the water passing through the filters. This dissipation tank had a residence time of 18 min. The design specifications for the ozone contactor used in Phase I are given in Table A-5

Table A-5
Ozone Contactor 2 Design Specifications

Parameter	Value
Height	3113 mm
Inner diameter	225 mm
Outlet diameter	2863 mm
Contactor volume	123.7 L
Contact height	2863 mm
Contact volume	113.8 L
Contact time	16.3 min
Design flow	7.2 L/min
overflow rate	< 1 L/min
Diffuser height	106 mm
Diffuser porosity	'C'
Diffuser diameter	120 mm

Ozone was produced from pure oxygen (99.6% minimum purity; <10 ppm moisture; <50 ppm THC as CH_4). Six oxygen cylinders were stored on the first floor of the Recal building. A combination of 1/4 inch Teflon® and stainless steel tubing routed the oxygen from the pressure regulators on the cylinders to the pilot plant location on the fourth floor. A discharge pressure of 30 psi was maintained on the regulators since 15 psi was required to efficiently operator the ozone generator. Oxygen intake lines were required for both ozone generator and ozone monitor (as a zero reference gas).

Ozone Generator

The ozone generator used initially was a Union Carbide laboratory size generator (Linde model SG-40-60). This unit was replaced in January 1993, primarily due to safety concerns when large ozone leaks and a reduction in efficiency were noted. This unit was replaced with PCI ozone generator, Model GL-1. This model produced 2.4 pounds/day ozone at three percent concentration by weight when oxygen was used. The generator received oxygen from the oxygen cylinders and the flowrate was control by an exterior flowmeter to maintain an operating pressure of 15 psi. A cooling water was pumped into the generator to cool the ozone cell and subsequently flowed out of the generator to waste. The generator was operated at the zero power level which produced approximately one percent ozone concentration by weight. The ozone exiting the ozone generator was controlled by an exterior flowmeter which was adjusted according to dosage requirements.

A description of the major operating components of this unit are as follows: The unit utilized a cell constructed of a stainless steel electrode and a silver plated glass electrode which were surrounded by a PVC shroud. Dry oxygen passed through a gap between the stainless steel and glass electrodes. There was a cooling water inside the stainless steel electrode and H.V. Coolant between the glass electrode and the PVC shroud to cool the cell. A high voltage discharge through the dry oxygen causes the oxygen in the feed gas to be converted to ozone.

Ozone Monitor

The purpose of the ozone monitor was to measure with great accuracy the percent by weight of ozone in the gas stream passing through the diffuser. The ozone monitor used in this study was a PCI, Model HC-NEMA 12. The instrument utilized a UV adsorption ozone photometer to measure ozone concentrations which ranged from 0.000 to 9.999 percent by weight. The sampling system consisted of an inlet needle valve for the sample and zero gas, a flowmeter, a solenoid valve and a sample chamber. Depending on the position of the solenoid valve, zero or sample gas was force through the solenoid valve, the sample chamber and flowmeter. The intensity of the UV light traversing the sample chamber was attenuated as prescribed using Beer's Law. The ratio of the intensities were determined and results processed by the microcomputer to determine the ozone concentration and was displayed on the digital readout.

Oxygen from the cylinders on the first floor was directed to the ozone monitor for the zero reference gas, and controlled by a flowrate at 1.0 L/min. When the ozone gas concentration in the contactor stream was required, a valve was opened to divert gas flow to the ozone monitor. Pressure adjustments were completed to maintain a pressure of 15 psi in the generator. A digital reading was obtained that always closely correspond to the one percent by weight indicated on the ozone generator readout.

Ambient Ozone Monitor

A Mast, Model 727-3, ozone monitor was used to monitor background or ambient ozone air conditions in the pilot plant room. The unit employed a UV absorption ozone photometer to measure ozone concentration readings digitally ranging from 0.00 to 9.99 ppm. A sample gas was continually supplied to the sample chamber by a self contained pump and sample handling system. The intensity of the UV beam traversing the sample cell was attenuated in proportion to the concentration of ozone in the sample as prescribed by Beer's Law. The signal was detected and electronically processed. An alarm system provided a signal when concentrations exceed the desired ozone threshold valve (0.2 ppm). This instrument was also used to measure the off-gas concentrations from the ozone contactor to determine the transfer efficiency of the system.

The ozone generator, ozone monitor and discharge flowmeter were all housed in a fume hood, to protect the pilot plant room from exhaust ozone gas. The fume hood was located in the north-west corner of the pilot plant room (Figure A-2). The fume hood was designed with a four inch diameter vent pipe connected to an outside wall. The pipe contained a blower to purge the system of ozone on a continual basis. An interlock was installed such that if the ambient ozone levels exceeded 0.20 ppm an alarm would be triggered from the ambient ozone monitor and the ozone generator and monitor would be automatically shut off. A data recorder was connected to record the ambient ozone levels and provide a record of the time if the ozone generator was shut off

Ozone dosage was based on a 1:1 ratio of ozone to NVOC (in the settled storage water), however this criteria was modified to a ratio of 0.75, when a target ozone residual of 0.1 in the contactor effluent was desired to optimize biofilm development.

Dual Media Filtration

Design

The filter columns were fabricated from three standard sections of 150 mm heavy-wall glass pipe with standard conical flanges. The segments were jointed with Teflon® gaskets and flange clamps, and had a combined height of 4.2 m. The base section had a cone-shaped bottom and a backwash inlet connection directed downwards towards the apex of the cone. This enabled a uniform backwash flow distribution. Three sample ports were provided to sample both water and filter media from depths which intersected the sand, anthracite coal (GAC F-300 in Filter 4) and interface of the two media. The sample port design consisted of a 3/4 inch glass port attached to the glass column. A Teflon® plug was constructed to tightly fit the glass port and an "o: ring" and external clamp were used to securely fasten the Teflon® plug to the glass port. The Teflon® plug was constructed with a 1/4 inch hole through the centre to accommodate a stainless steel tube with a sampling valve attached on the outside end. A screen was attached to the inside end of the tube, which extended 50 mm into the column. The tube was fastened to the Teflon® plug by a fitting that screwed into the plug so that the tube could be easily removed to occasionally sample filter media.

Operation

After the pre-oxidation step the water was split into five streams. Filter 1 was a chlorinated stream and was operated at a hydraulic rate of 10 m/hr. Filters 2,3 and 4 were pre-ozonated streams and operated at a hydraulic rate of 10, 5 and 5 m/hr respectively. The fifth filter received no pre-treatment and was operated at 10 m/hr. Water was pumped from the pre-oxidation tanks to the dual-media filters by small, constant speed centrifugal pumps (March Mfg. Inc., Glenview, IL, Model TE-MDX-MT3). Flow to the filters was controlled by manually adjusting globe valves on the pump discharge lines and monitored using calibrated Gilmont® rotameters (Cole-Parmer Instruments Co., Chicago, IL.). The filter feed pumps discharged to a vented inlet standpipe system through a perforated stainless steel cap. The discharge location was at a depth slightly above the filter media. As both suction and discharge heads were constant, flow to the filters remained constant, enabling the filters to operate in the constant rate, variable head mode.

The filter media was supported by a 100-mesh stainless steel screen, reinforced on both sides by perforated stainless steel plates between the faces of the bottom flanges. This plate was also intersected with a stainless steel tube to discharge air during the air scour step during backwash. The filters discharged to rectangular weirs elevated above the top of the bed surface to prevent filter dry-up. The individual weirs were split and provided an overflow which was run to waste. The weirs also functioned as a sampling location and acted as a constant head to feed the GAC pumps.

The dual media consisted of 12 inches (300 mm) of gravel layered in a reverse grade. Overlying the gravel was 12 inches (300 mm) of sand and 24 inches (600 mm) of anthracite coal and F-300 in the case for filter 4. The design provided an empty bed contact time of 11.0 and 5.5 min for a hydraulic loading rate of 5 and 10 m/hr respectively. The specific design specifications for the dual media filters are provided in Table A-6.

Table A-6

Dual Media Filter Design Specifications

Parameter	Value
Gravel (Depth and Mesh size)	
100 mm (4 in)	3/4" x 1/2" mesh
50 mm (2 in)	3/16" x 3/8" mesh
50 mm (2 in)	sieve #4 x sieve #10
50 mm (2 in)	3/16" x 3/8" mesh
50 mm (2 in)	3/4" x 1/2" mesh
Anthracite (filters 1,2,3, & 5)	
Depth	600 mm (24 in)
Effective Size	1.18
Uniformity Coefficient	1.3
GAC F-300 (filter 4)	
Depth	600 mm (24 in)
Mesh size	8 x 30
Iodine No. (min)	1027
Abrasion No. (min)	83.6
Moisture (max)	0.49 %
Ash (max)	6.56 %
Sand (all filters)	
Depth	300 mm (12 in)
Effective Size	0.44
Uniformity Coefficient	1.4
Hydraulic Loading Rates	
Columns 3 and 4	5 m/h
Columns 1,2 and 5	10 m/h

Backwashing

Backwashing of the dual media filters was required every 24 hours. The backwashing procedure employed both air scour and water. The design of the air scour system utilized instrument air available at the Rossdale water treatment plant, which had under gone a preliminary drying cycle. The air source was intercepted outside the pilot plant room and was monitored inside by a flowmeter with a control valve (FM-1000, Matheson, Montgomeryville, PA) . A Billard airline filter cartridge (Levitt Safety, Edmonton, AB) was purchased and installed to remove any additional organic material from the compressed air. The clean air was further split into five streams using stainless steel tubing, and Teflon® tubing was used to route the line through the underdrains of the dual media columns. The backwash water supply was drawn from each individual storage tank to avoid cross-contamination. Two pumps were used in series and controlled by a globe valve.

Backwashing was completed daily at approximately 10:00 am. Initially the influent and effluent pumps were turned off and the column was drained to 2 to 3 inches (50 to 75 mm) above the media. Next, the stored treated water was backwashed through the column at a low rate and the air scour was started at this time. The water flowrate was 6.2 gpm/sf and the air rate was 3 scfm/sf for 4 minutes. After this stage, the backwash and air scour was turned off for 100 second. Following this lag period the backwash water flowrate was turned up high to achieve 20 percent bed expansion. This step was continued for approximately 5 minutes until the water was clear.

Granular Activated Carbon Contactors

Water was pumped from the effluent weir boxes to the GAC columns by a system similar to dual media feed system. Four GAC columns were available and had the identical design and operation as the dual media filters, with the exception of five sampling ports evenly spaced along the depth of the columns. Bed depths were variable up to 2.3 m. Sample ports were installed at the various depths throughout the bed to allow for sampling at empty bed contact times varying from 1 to 35 min depending on hydraulic loading rate. Effluent of the columns flowed to weir boxes by gravity and drained into each individual backwash storage tanks. A fifth storage tank located above the four backwash storage tanks and was used to storage chlorinated backwash water from stream 1. The tank consist of four small tanks joined by exterior piping and a standpipe with an overflow to control the head in the tank. This water was only used to backwash filter 1. The GAC contactors were backwashed for 15 min once a week at a flowrate to obtain a fluidized bed expansion of 20-35 percent. Design specifications for the GAC contactors are displayed in Table A-7.

Table A-7
GAC Contactor Design Specifications

Parameter	Value
Carbon	
Type (Column 2,3 75)	F-400
Effective Size	0.55-0.75 mm
Sieve Size	12-14 (US standard)
Iodine Number	1,050 (minimum)
Pore Volume	0.94 cc/g
Uniformity Coefficient	1.9 (maximum)
Particle density wetted-water	1.3-1.4 g/cc
Total surface area (N_2 BET)	1050-1200 mm^2/g
Type (Column 3)	PICA
Bed depth	
Column 2,3,4 and 5	2.3 m
Empty Bed Contact Time	
Column 3 and 4)	1-34.5 min
Column 2 and 5)	1-17.3 min
Hydraulic Loading	
Column 3 and 4	4 n/h
Column 2 and 5	8m/h

Construction of the dual-media filters and GAC columns presented major difficulties. Several of the glass column sections fractured during erection, and during transport to Edmonton, in the case of Filter 1. For the GAC columns sealing, the stainless steel fitting (for sample ports) to the walls of the columns was a major problem which caused considerable construction delays. Adequate seals were eventually achieved by the use of foamed Teflon® tape on the inside of the fittings and a combination of Teflon® tape wrapping and silicon caulking on the outsides. A better design was developed for the dual media filters as described in section 8.0.

Maintenance

Prior to the initiation of the Phase I experiments all surfaces were cleaned with a solution of 5 percent hydrochloric acid. Monthly, the settled water storage tank, clarifier, flocculation, and pre-sedimentation tanks were drained and cleaned with Rossdale service water (non-chlorinated). This practice removed sludge build-up but also removed mud that often built up on the side of these surfaces. All flowmeters and flocculator motor drives were frequently calibrated to ensure all design criteria were being met.

Pilot Plant Performance

A large amount of date was collected daily in addition to backwashing and other plant activities. The data included turbidities, pH, temperature, flowrates, headloss, colour, and ozone and chlorine residuals. An example of typical daily data collection is given in Tables A-8 to A-11.

Table A-8: Typical Daily Operational Data for Pre-Treatment Step

Date: Nov. 23, 1992
Time: 8:30 am
Recorded by: M.J.M

	Raw	Floc 1	Floc 2	Floc 3	Clarifier	Settled Water	Chlorine	Ozone
Water Flow (L/min)	38.43	30.86	30.86	30.86	30.86	19.97	4.69	7.19
Temperature (°C)	5.80	5.90	5.90	6.80	6.80		6.90	7.80
Turbidity (ntu)	3.75	4.45	15.10	4.50	1.10		1.25	1.50
pH	8.08	7.80	7.79	7.78	7.76		7.85	7.81
Colour (tcu)	2.00	-	-	-	-		-	-
NVOC (mg/L)	2.07	-	-	-	-		-	-
Residual (mg/L)	-	-	-	-	-		0.55	0.10
Motor Drive Speed	-	25.00	14.50	12.50	-		-	-
rpm	-	40	20	12	-		-	-
Waste Flow (L/min)	7.57	-	-	-	10.99		-	-

Table A-9: Typical Daily Operational Data for Ozone System

Date: Nov. 23,1992
Time: 8:30 am

Ozone System	Contactor #1	Contactor #2
Water Flow Contactor (L/min)	-	7.19
Oxygen Flow (L/min)	-	2
Power Setting (w)	-	0
Ozone Flowmeter	-	10
Ozone Gas Flow (L/min)	-	0.32
Desired Dose (mg/L)	-	1.88
Influent Conc. (%w/w)	-	1.10
Off Gas conc. (ppm)	-	0.85
Transfer Efficiency (%)	-	94.6
Blank	-	0.225
Ozone Sample Absorbance	-	0.185
Difference in Absorbance	-	0.004
Residual Ozone conc. (mg/L)	-	0.096

Table: A-10 Typical Daily Operational Data for Coagulant System

Aluminex Feed	
Raw Flow (L/min)	30.86
Dose (mg/L)	22.0
Aluminex sp.gr.	1.21
Stock Conc (%)	100
Speed Setting	1.2
Q (ml/min)	0.59

Table : A-11 Typical Daily Operational Data for Dual Media Filters and GAC

Dual-media Filters	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5
Q (m/h)	10.17	9.55	4.25	4.94	9.27
Flowmeter Reading	69	72	38	40	70
Water Level (mm)	2410	2770	1770	2060	2420
Headloss (mm)	1210	1570	570	860	1220
Turbidity (ntu)	0.58	0.60	0.20	0.18	0.54
pH	7.81	7.78	7.79	7.80	7.82
Temperature °C	7.20	8.10	8.70	8.20	7.30
Backwash Time	10:15	10:00	9:45	9:30	9.25
GAC Contactors	GAC 1	GAC 3	GAC 4	GAC 5	
Q (m/h)	8.03	3.83	3.91	7.97	
Flowmeter Reading	59	63	33	58	
Water Level (mm)	-	-	-	-	
Headloss (mm)	-	-	-	-	
Turbidity (ntu)	0.23	0.21	0.21	0.21	
pH	7.89	7.76	7.68	7.54	
Temperature °C	8.90	9.70	9.10	8.20	
Backwash Time	-	-	-	-	

Overall pilot plant performance during phase I experiments was very good. Typical raw water turbidity levels range from 2 to 20 ntu, with temperatures ranging form 2 to 8 °C. The pH level are typical around 8.3 and decreased after coagulation to 7.9. The pH remains relatively uncharged through the remaining treatment steps. Coagulation and Flocculation performance had been optimized and a clarifier effluent turbidity was maintained < 1.0 ntu except during peak spring run-off events (≈ 2 ntu). The effluent turbidity from the dual media filters were typically 0.25 ntu for the low rate filtration (5 m/h) and 0.4 ntu for high rate filtration. The GAC effluent turbidity was rarely below 0.2 ntu.

Details of the GC/ECD analytical procedure for the determination for Haloacetic Acids, Trihalomethane Formation Potential, Choral Hydrate Formation Potential, Aldehydes and Oxo Acids are summarized in the following tables.

Table A-12
Haloacetic Acid Analysis GC/ECD Operational Details

Analytical Column	DB : 5.625 L : 30 m ID : 0.25 mm Film Thickness: 1.0 μm
Temperature Program	initial 50 °C (for 10 minute) rate 5 °C/minute final 250 °C (for 5 minutes)
Injector Splitless	Temperature: 157 °C Volume Injected: 2 μL Value open at 1 minute
Detector	ECD Temperature: 300 °C
Run Parameters:	Att 2^ = 3 cht speed = 0.5 area reject = 10 Thrsh = -3 Peak wd = 0.04 Run Length = 34.60 minutes
Internal Standard	1,2,dibromopropane at 100 μg/L

Table A-13
Trihalomethane Formation Potential Analysis GC/ECD Operational Details

Analytical Column	DB : 5.625 L : 30 m ID : 0.25 mm Film Thickness: 1.0 µm
Temperature Program	initial 50 °C (for 5 minute) rate 5 °C/minute final 200 °C (for 5 minutes)
Injector Splitless	Temperature: 220 °C Volume Injected: 2 µL Value open at 1 minute
Detector	ECD Temperature: 300 °C
Run Parameters:	Att 2^ = 3 cht speed = 0.5 area reject = 100 Thrsh = 1 Peak wd = 0.16 Run Length = 49.40 minutes
Internal Standard	1,2,dibromopropane at 100 µg/L

Table A-14
Chloral Hydrate Formation Potential Analysis GC/ECD Operational Details

Analytical Column	DB : 5.625 L : 30 m ID : 0.25 mm Film Thickness: 1.0 µm
Temperature Program	initial 50 °C (for 5 minute) rate 5 °C/minute final 200 °C (for 5 minutes)
Injector Splitless	Temperature: 220 °C Volume Injected: 2 µL Value open at 1 minute
Detector	ECD Temperature: 300 °C
Run Parameters:	Att 2^ = 5 cht speed = 0.5 area reject = 1000 Thrsh = 0 Peak wd = 0.04 Run Length = 40.20 minutes
Internal Standard	1,2,dibromopropane at 100 µg/L

Table A-15
Aldehyde Analysis GC/ECD Operational Details

Analytical Column	DB : 5.625 L : 30 m ID : 0.25 mm Film Thickness: 1.0 µm
Temperature Program	initial 60 °C (for 1 minute) rate 3 °C/minute final 280 °C (for 3 minutes)
Injector Splitless	Temperature: 220 °C Volume Injected: 2 µL Value open at 1 minute
Detector	ECD Temperature: 300 °C
Run Parameters:	Att 2^ = 4 cht speed = 0.5 area reject = 100 Thrsh = 1 Peak wd = 0.16 Run Length = 77.33 minutes
Internal Standard	1,2,dibromopropane at 100 µg/L

Table A-16
Oxo Acid Analysis GC/ECD Operational Details

Analytical Column	DB : 5.625 L : 30 m ID : 0.25 mm Film Thickness: 1.0 μm
Temperature Program	initial 60 °C (for 5 minute) rate 10 °C/minute final 280 °C (for 10 minutes)
Injector Splitless	Temperature: 250 °C Volume Injected: 2 μL Value open at 1 minute
Detector	ECD Temperature: 300 °C
Run Parameters:	Att 2^ = 6 cht speed = 0.5 area reject = 100 Thrsh = 1 Peak wd = 0.16 Run Length = 35 minutes
Internal Standard	1,2,dibromopropane at 100 μg/L

APPENDIX B

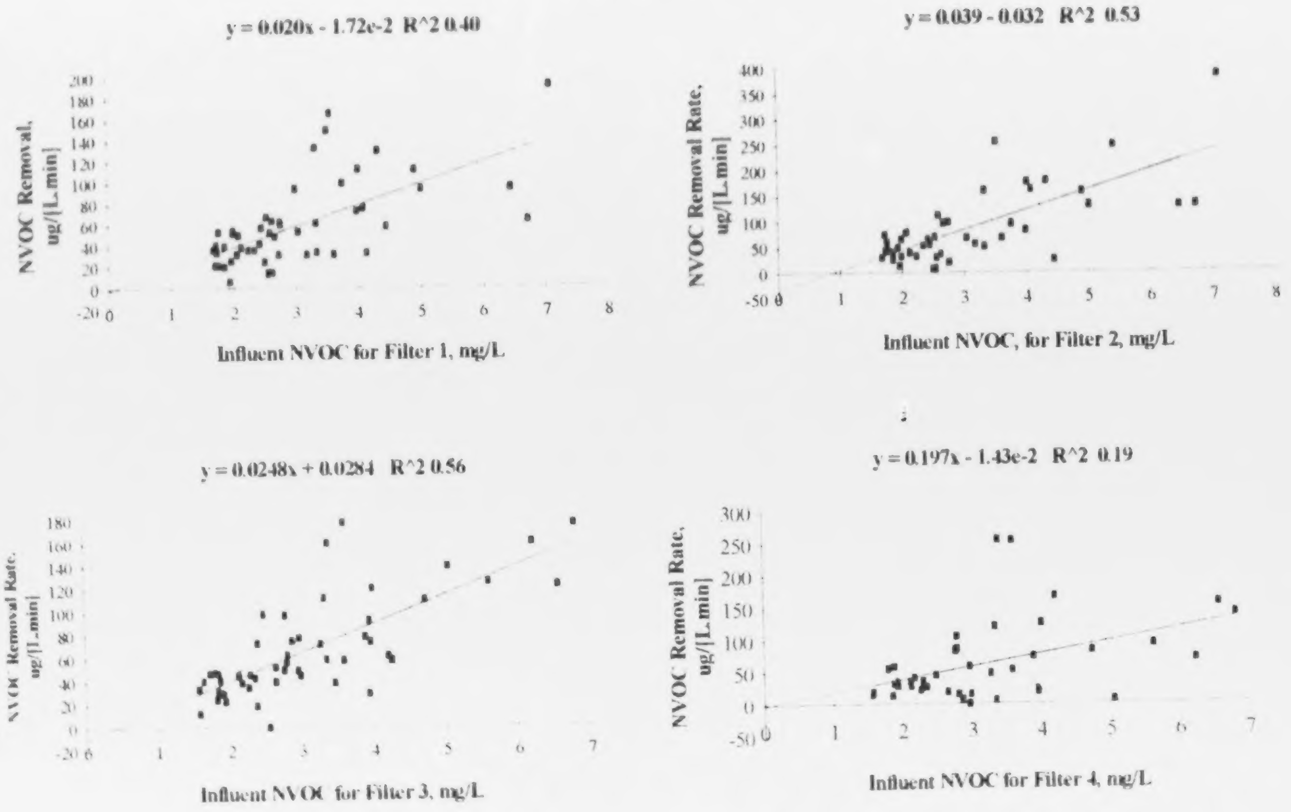


Figure B1 NVOC Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta 1989-1990

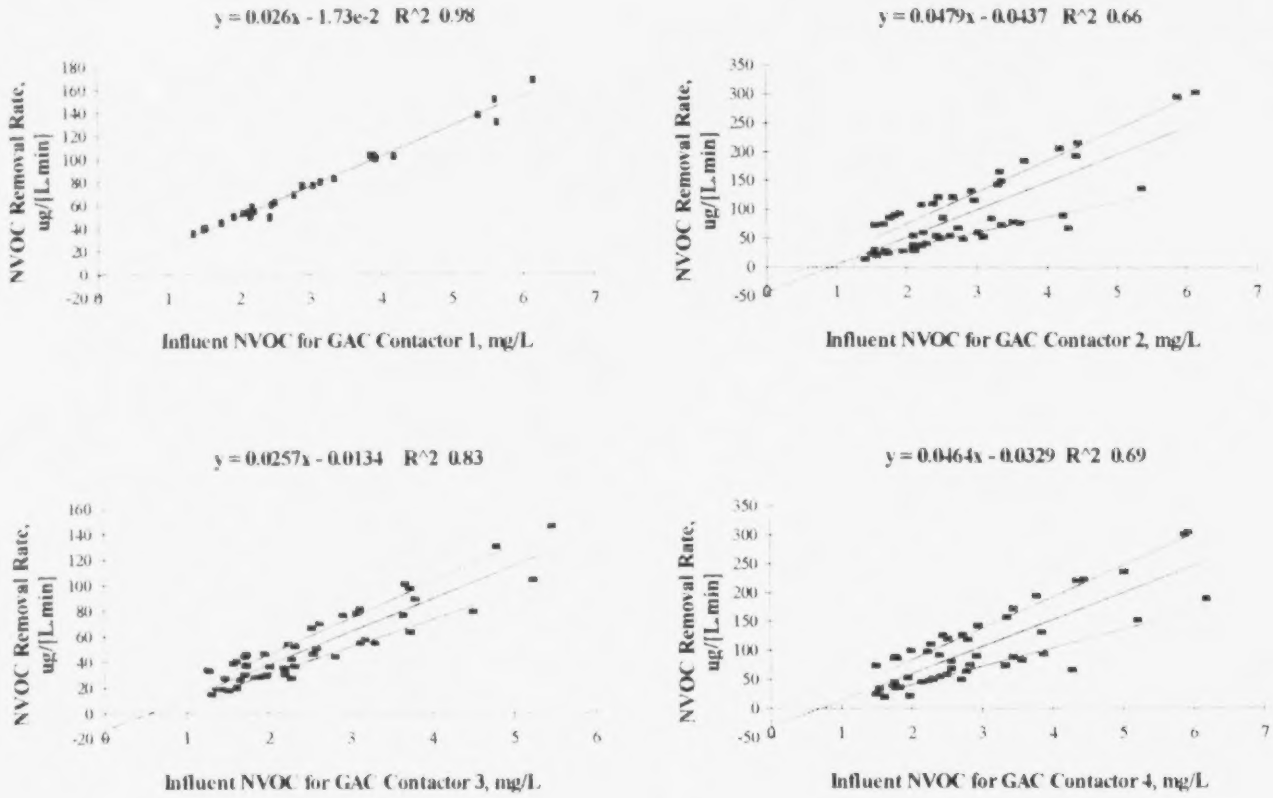


Figure B2: NVOC Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, 1989-90 Study

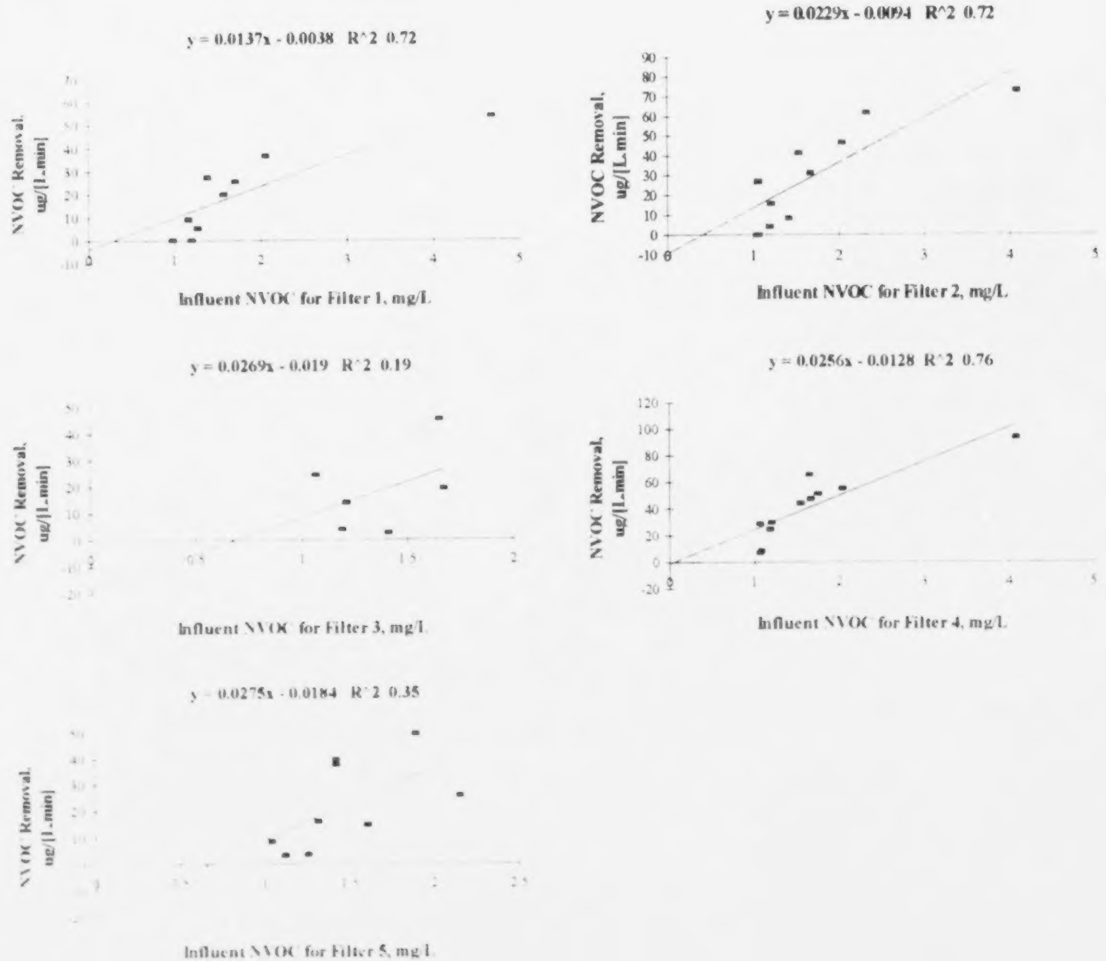


Figure B3 NVOC Removal Rate vs Influent Concentration for Filters, Edmonton, 1992-93 Study

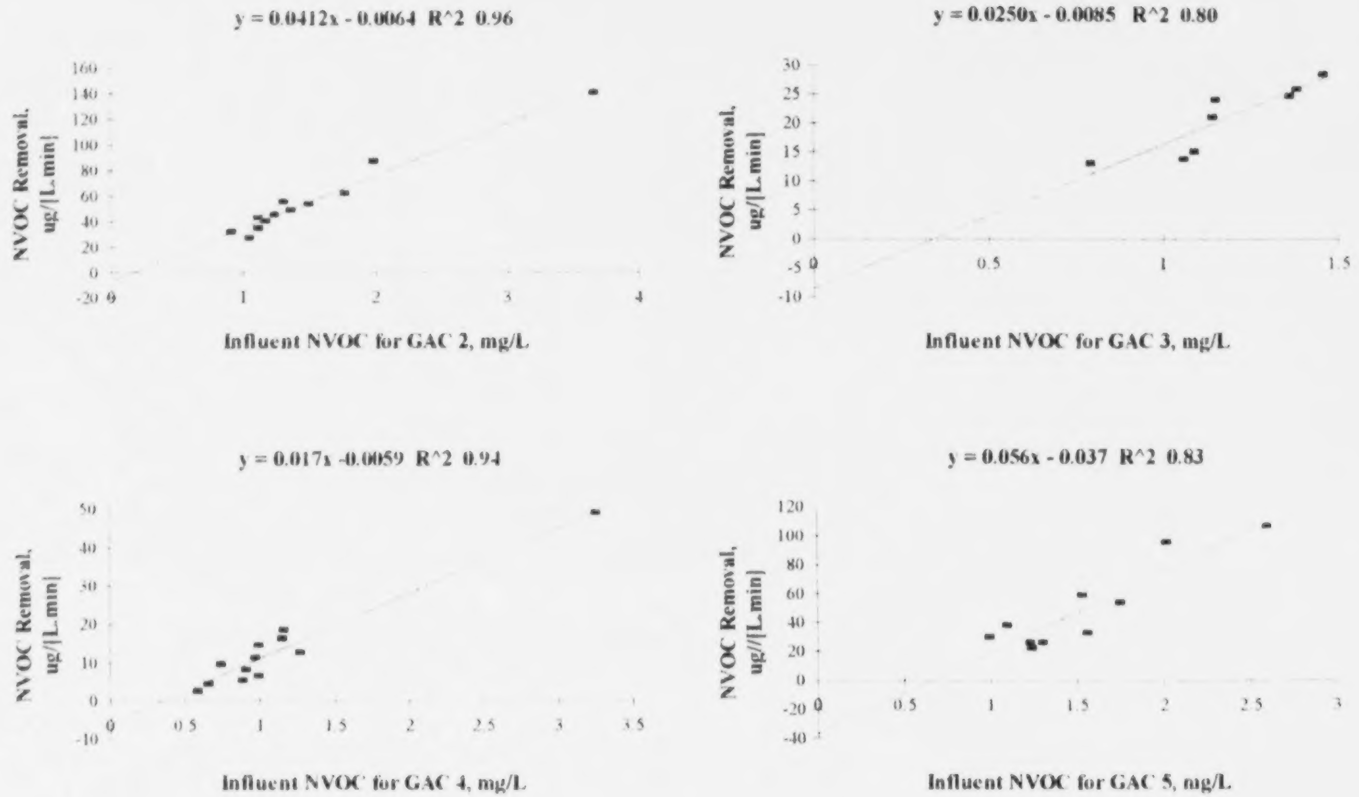


Figure B4 NVOC Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, 1992-93 Study

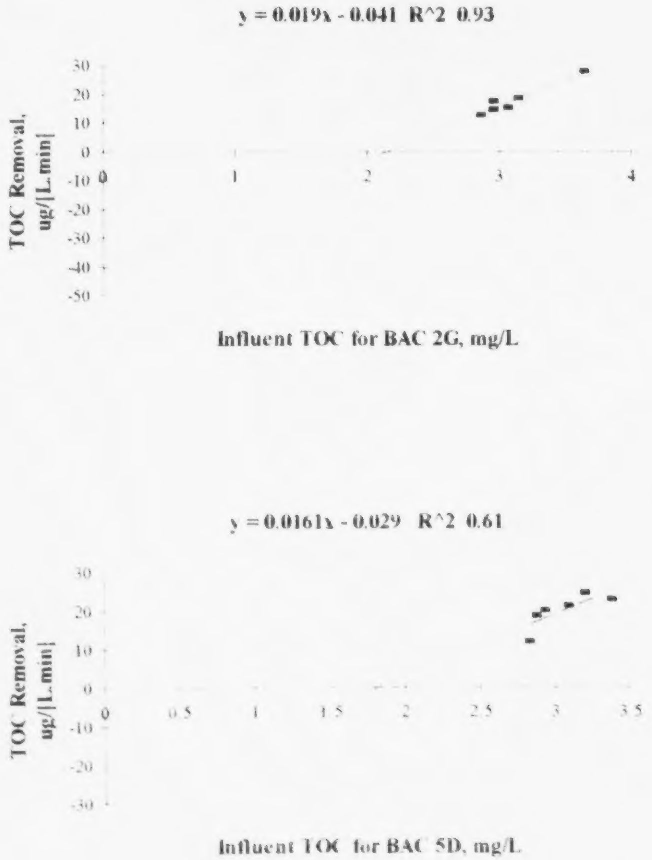


Figure B5 TOC Removal Rate vs. Influent Concentration for BAC Contactors, Laval, Quebec Study

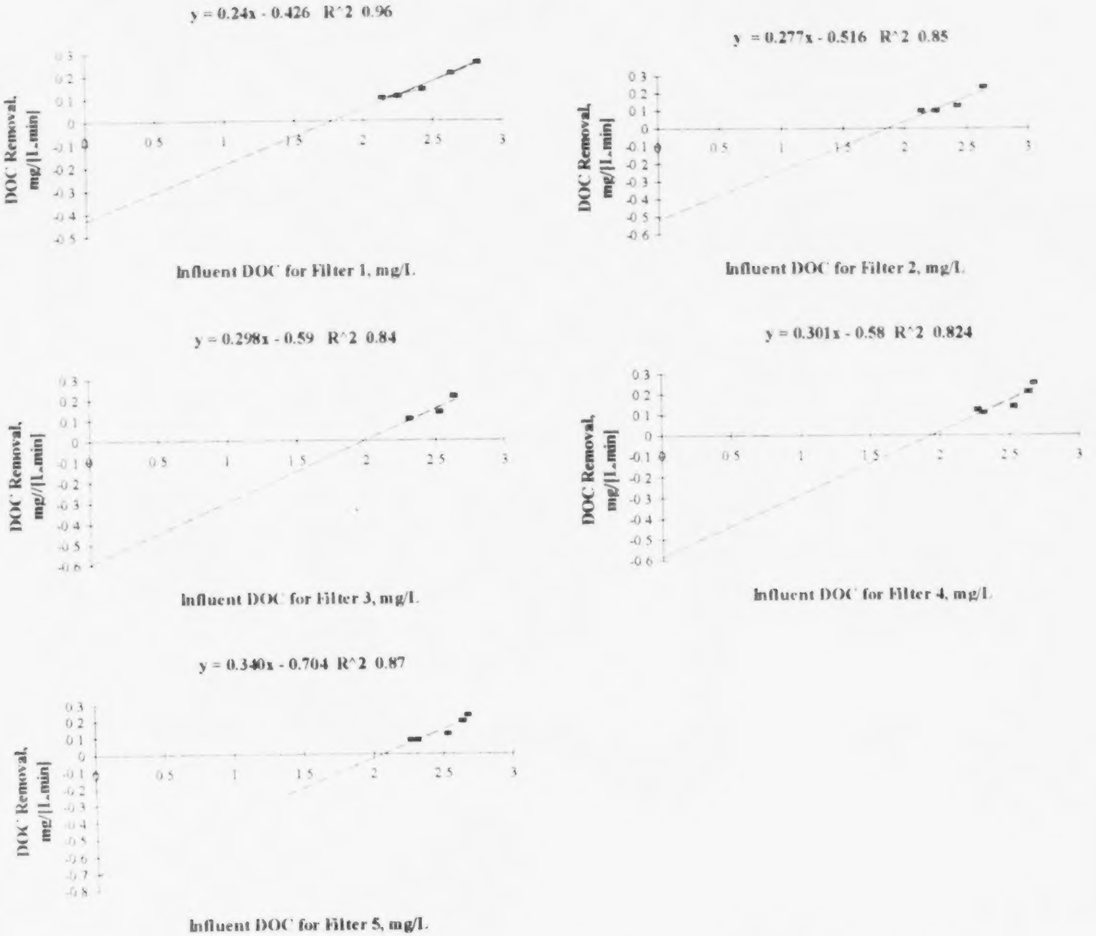


Figure B6: DOC Removal Rate vs Influent Concentration for Filters, Woodbridge, CT Study

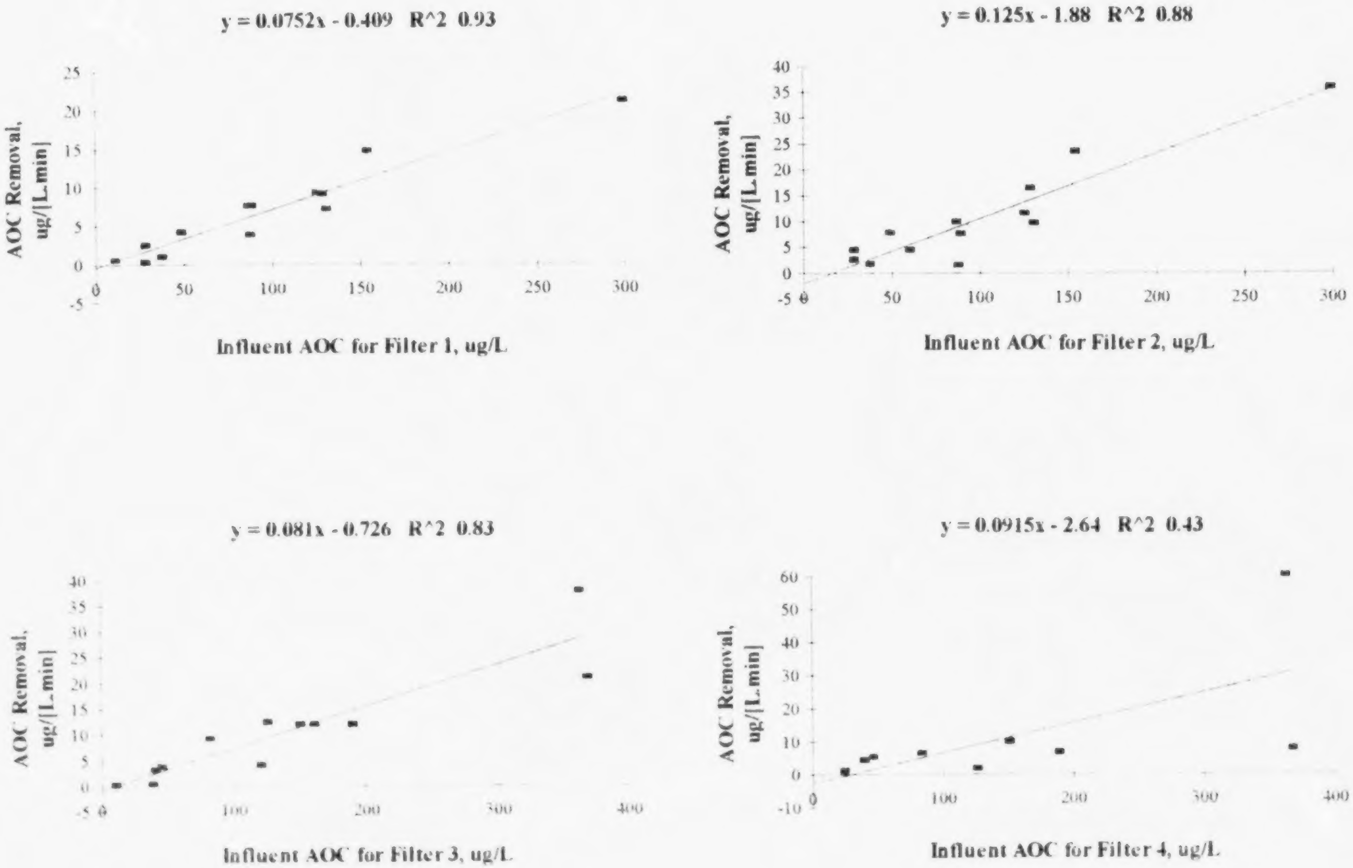


Figure B7 AOC Removal Rate vs. Influent Concentration for Filters, Edmonton, 1989-90

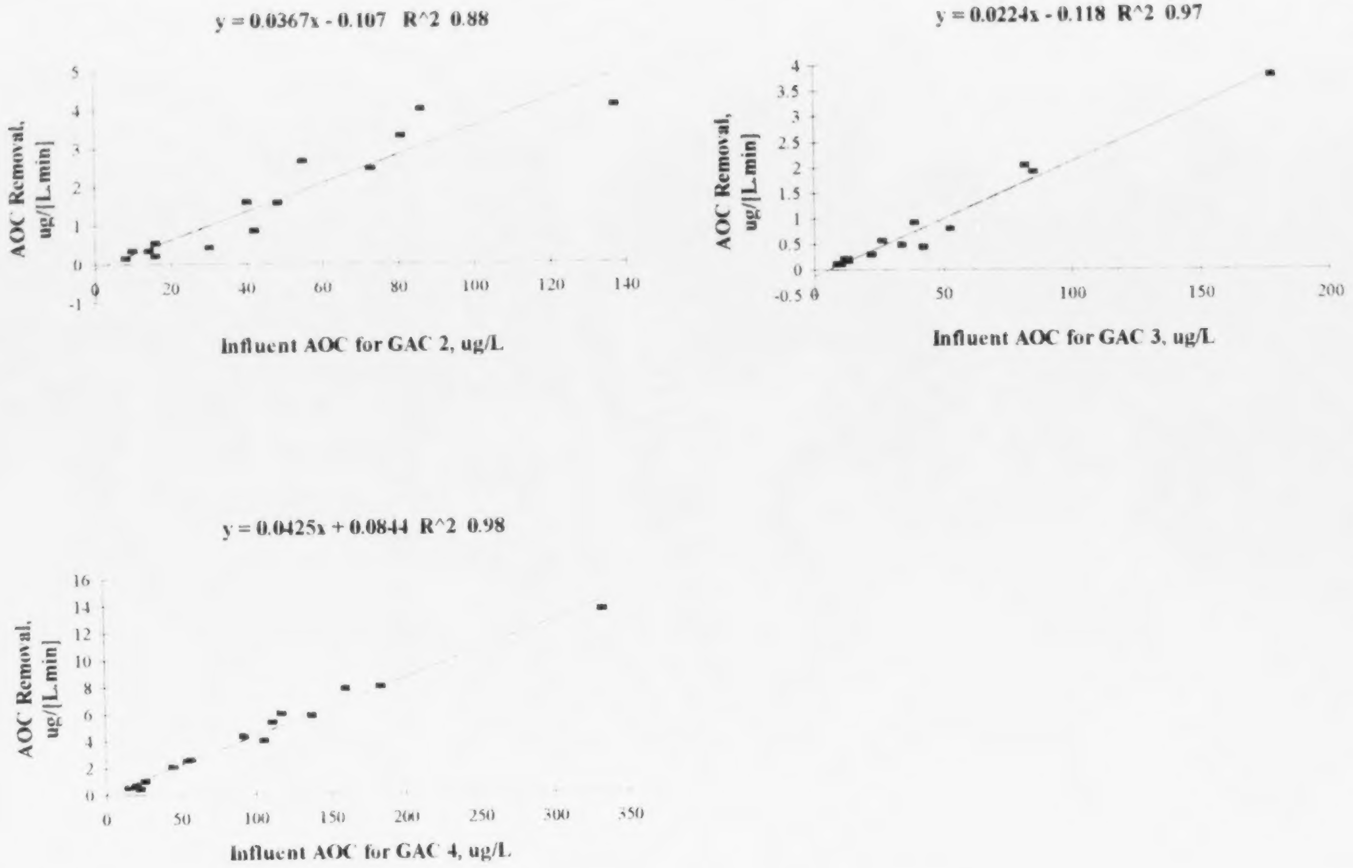


Figure B8: AOC Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, 1989-90

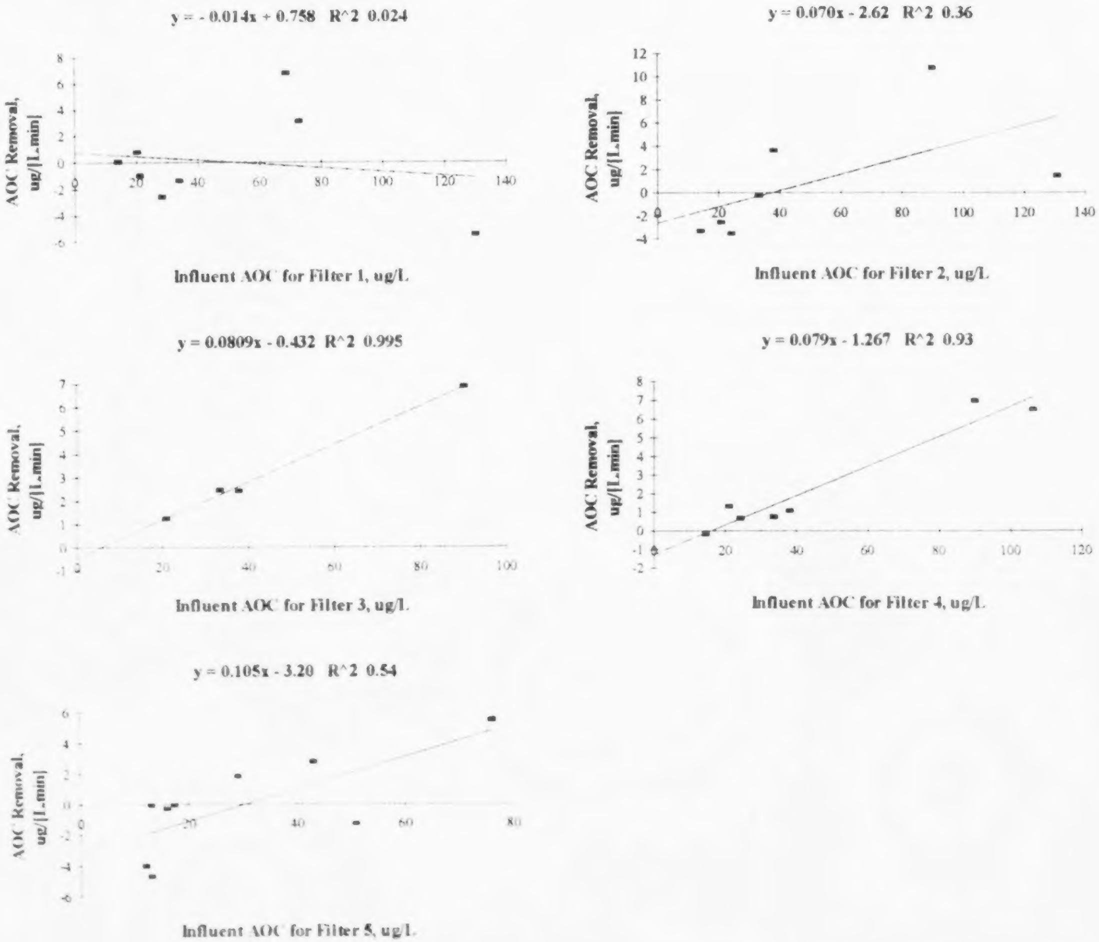


Figure B9 AOC Removal Rate vs Influent Concentration for Filters, Edmonton, 1992-93

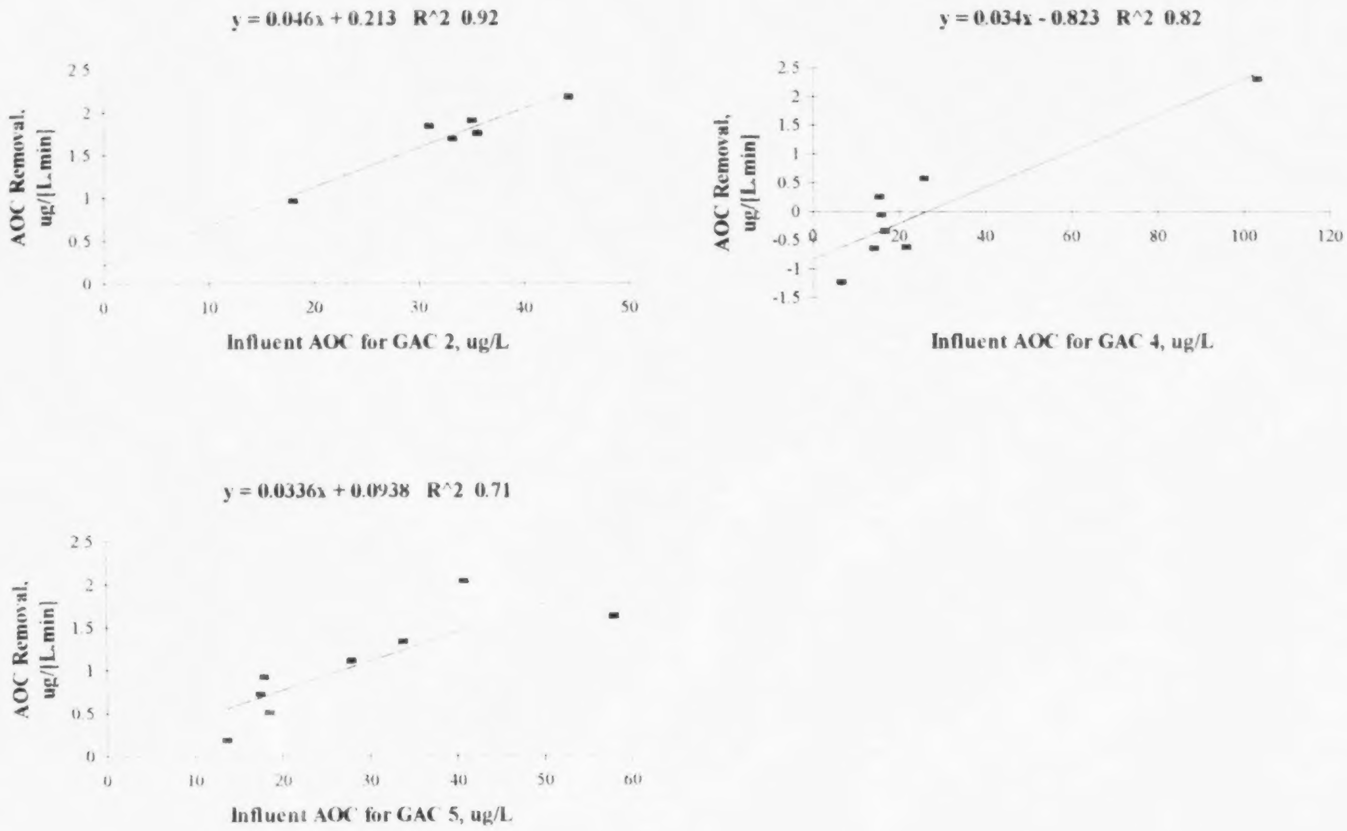


Figure B10. AOC Removal Rate vs. Influent Concentration for GAC Contactors Edmonton, 1992-93

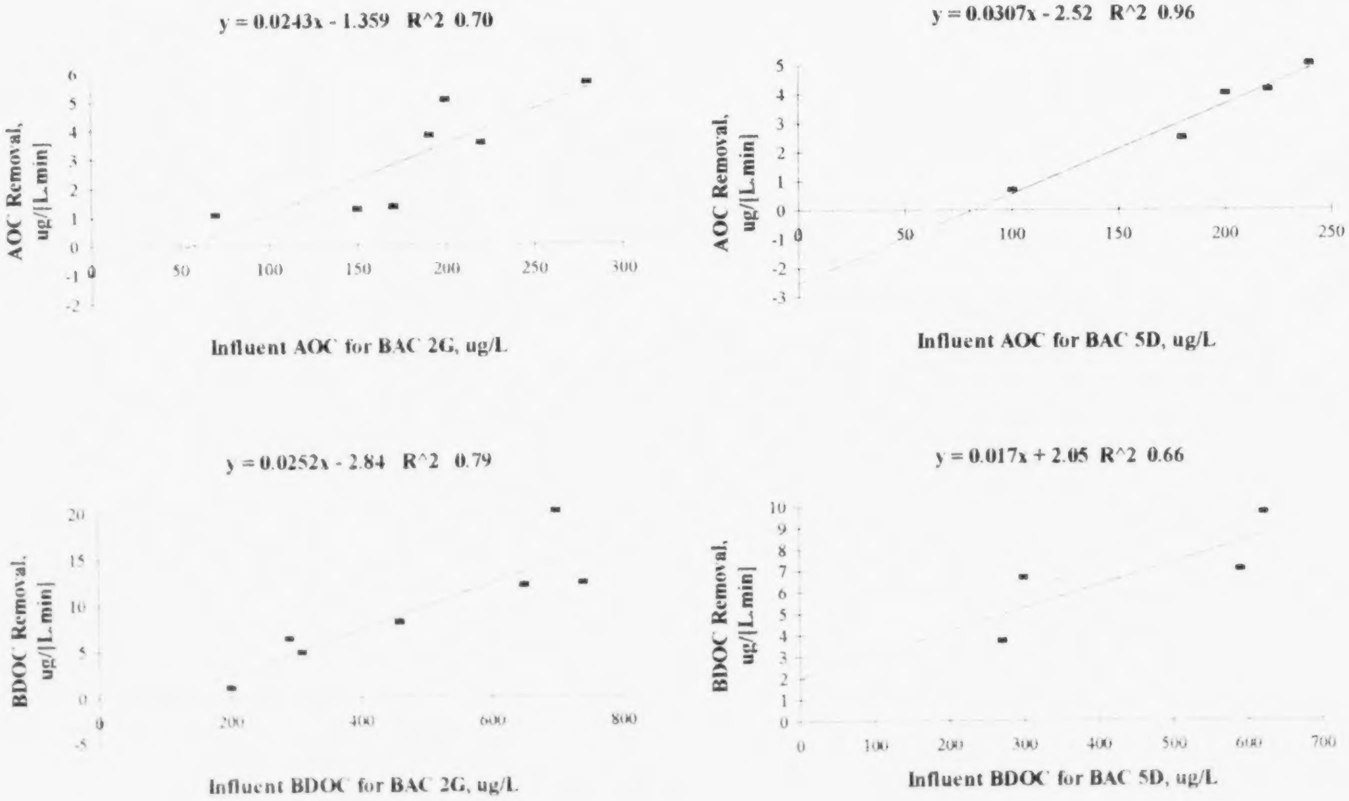


Figure B11 AOC and BDOC Removal Rate vs. Influent Concentration for BAC Contactors, Laval, Quebec Study

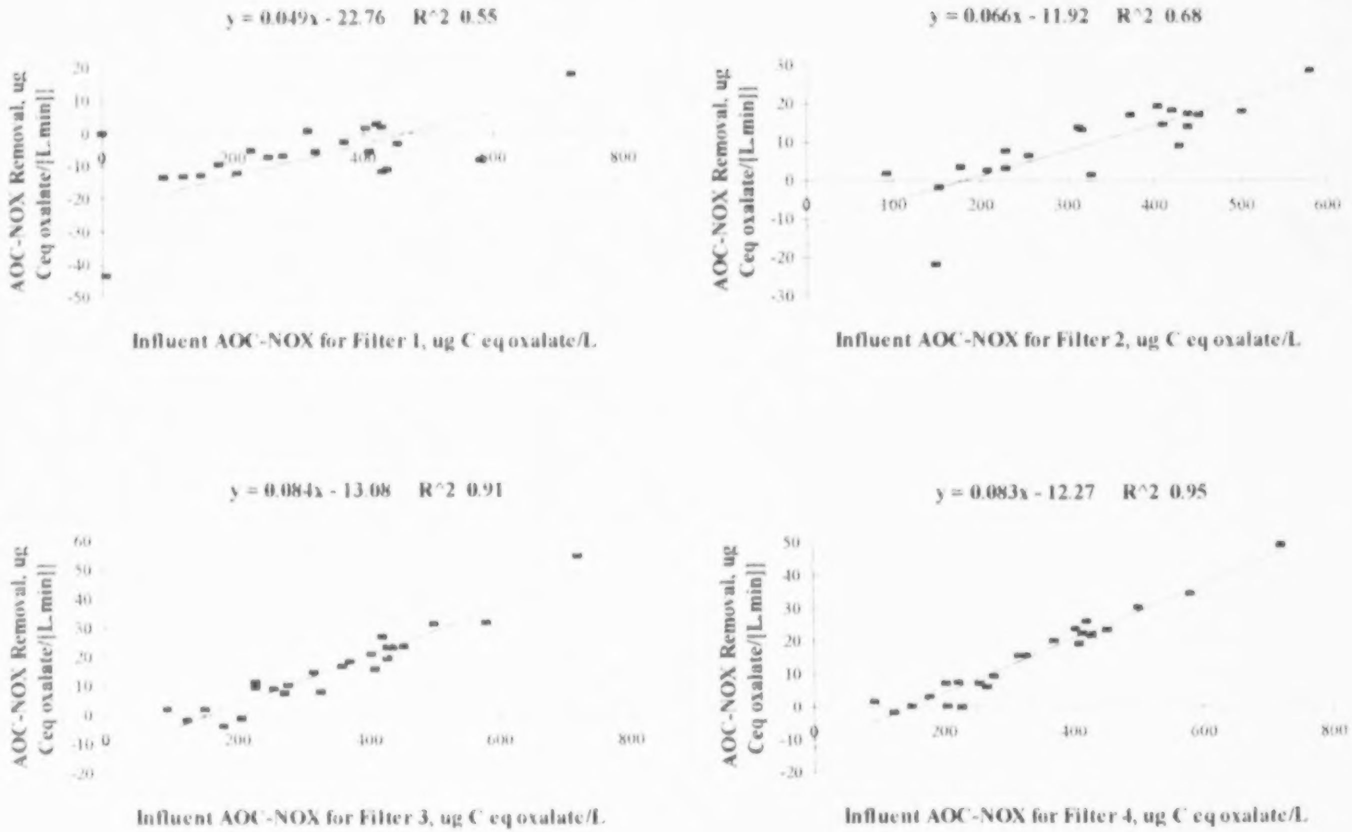


Figure B12 AOC-NOX Removal Rate vs. Influent Concentration for Filters 1-4, Cincinnati, Ohio Study

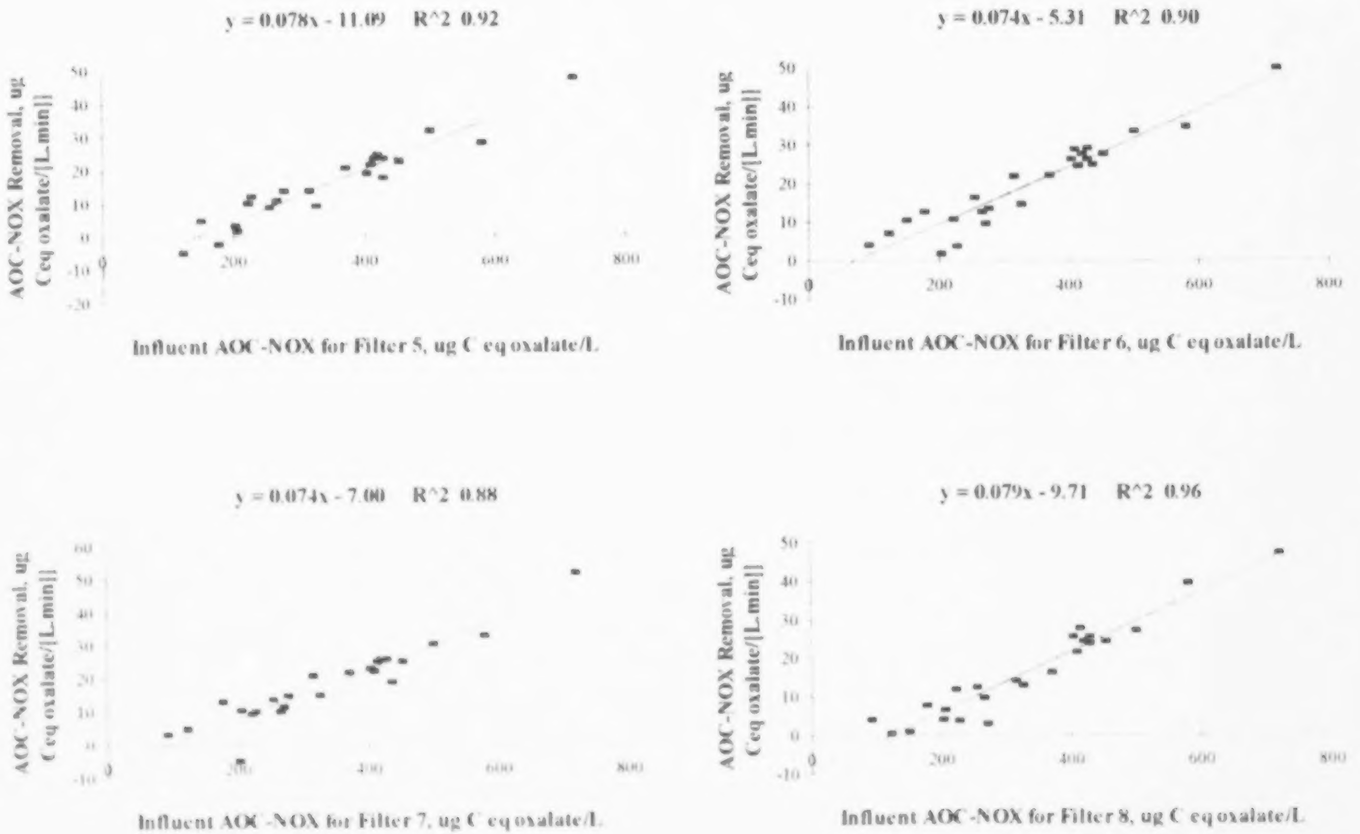


Figure B13 AOC-NOX Removal Rate vs. Influent Concentration for Filters 5-8, Cincinnati, Ohio Study

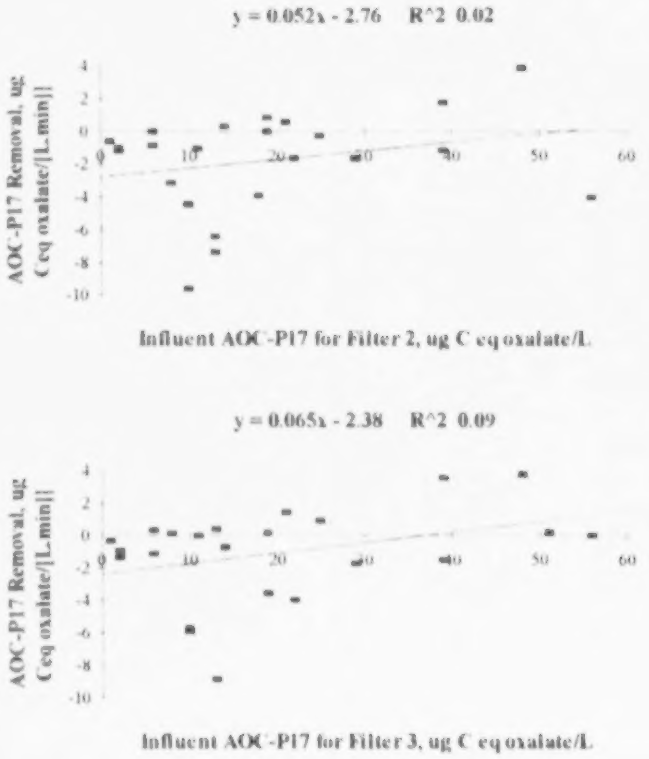


Figure B14 AOC-P17 Removal Rate vs. Influent Concentration for Filters 2 and 3, Cincinnati, Ohio Study

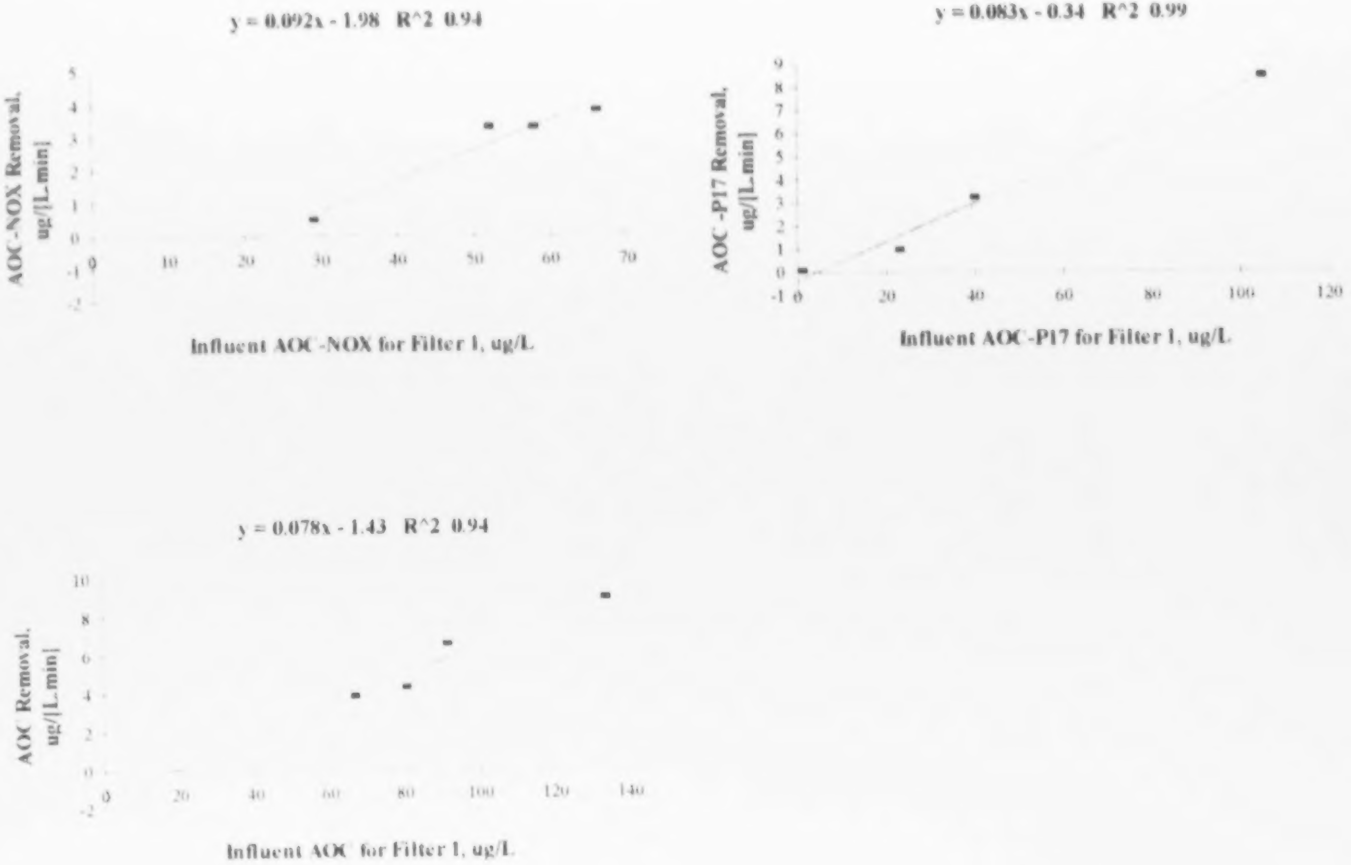


Figure B15 AOC Removal Rate vs Influent Concentration for Filter 1, Woodbridge, CT Study

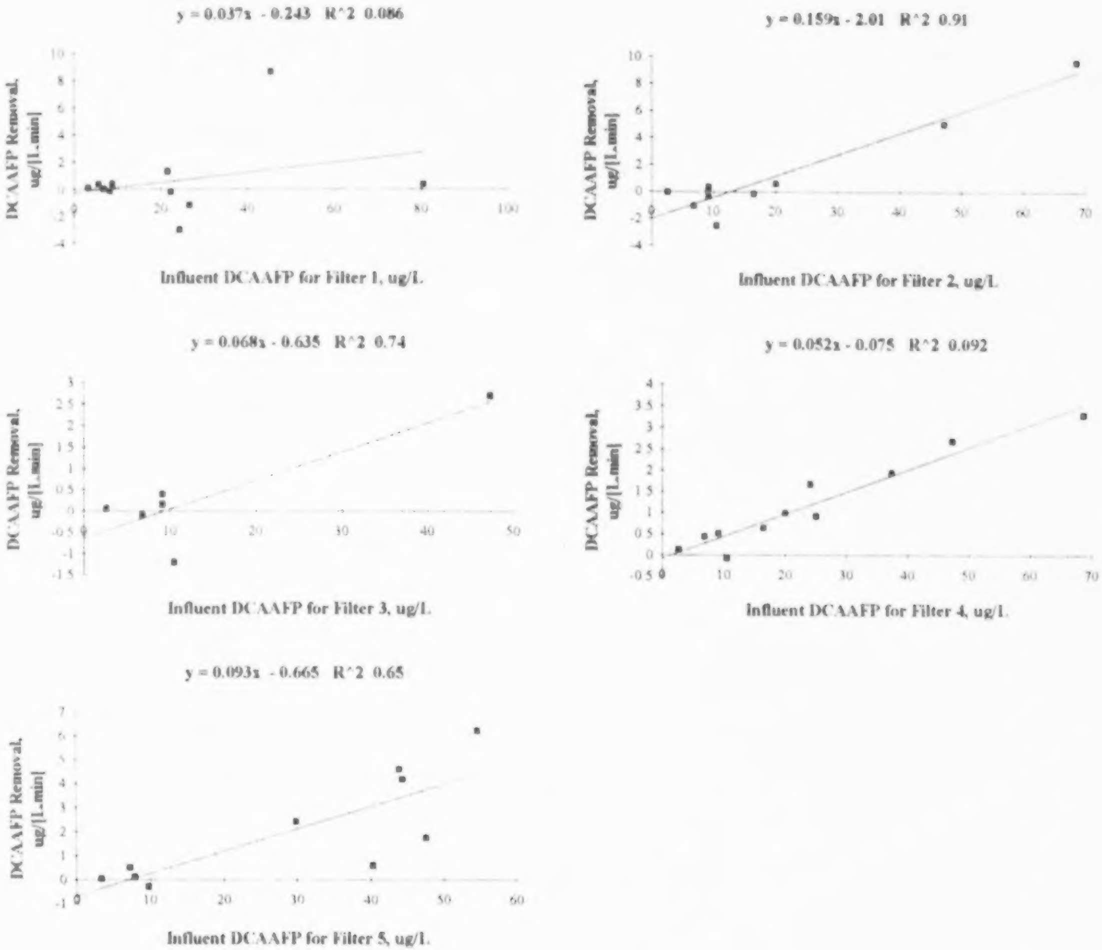


Figure B16 DCAAFP Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

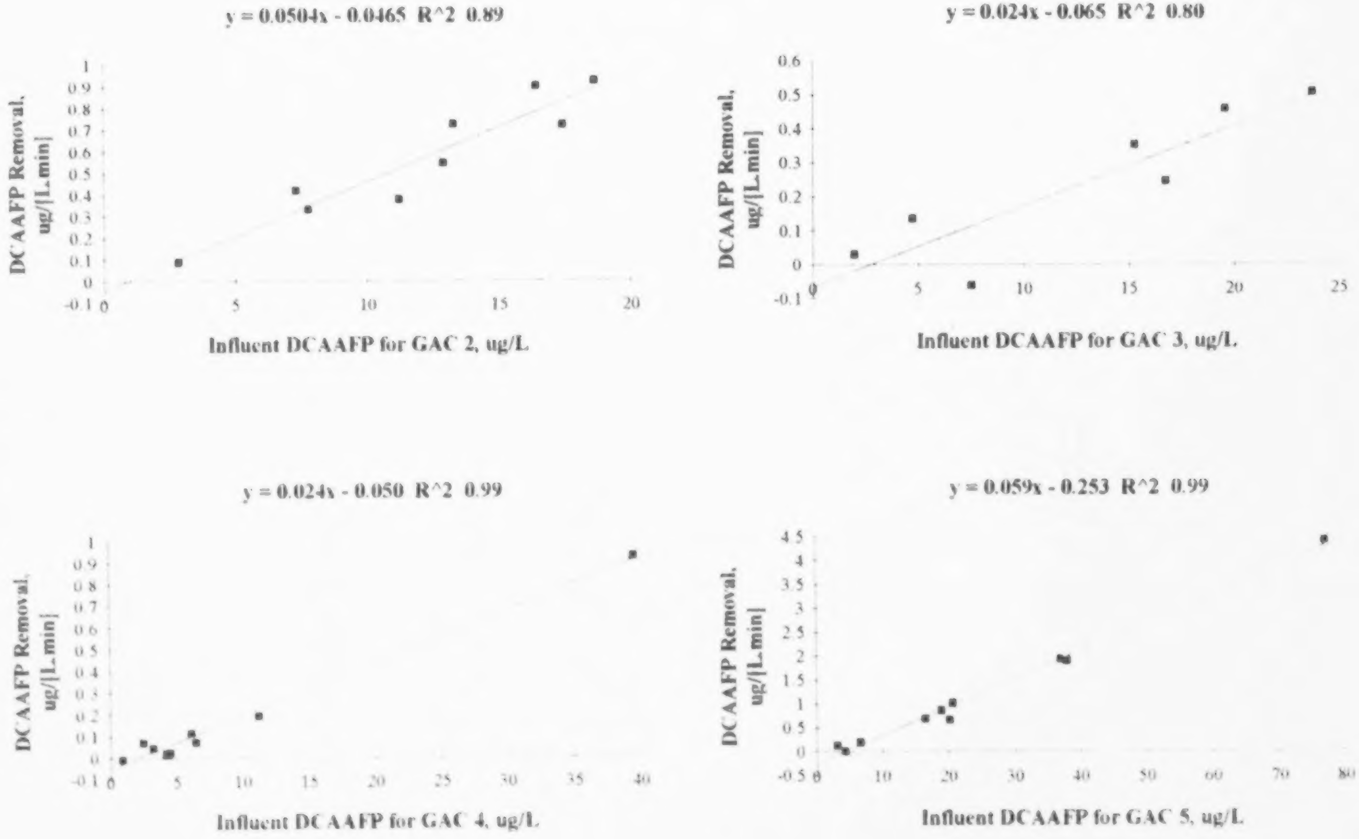


Figure B17 DCAAFP Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

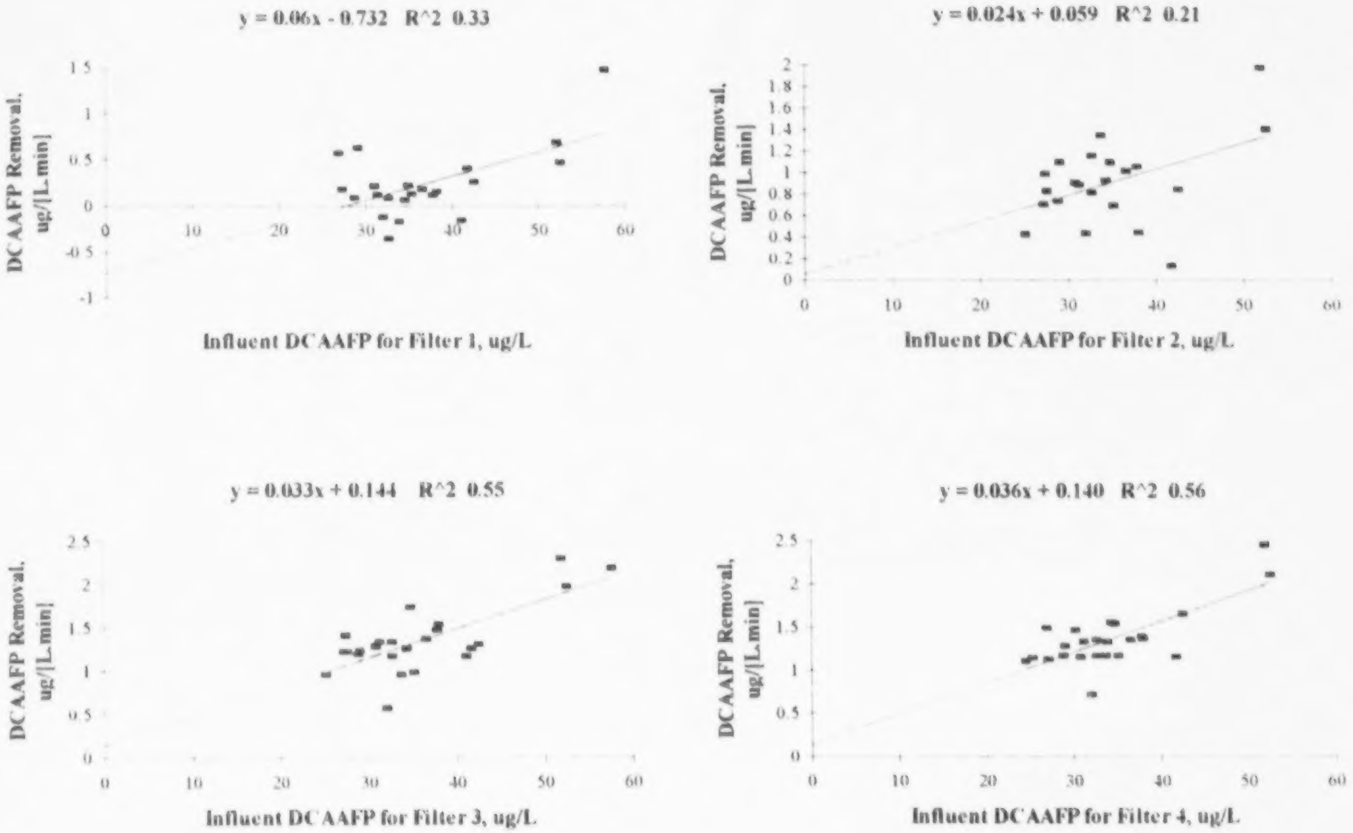


Figure B18: DCAAFP Removal Rate vs. Influent Concentration for Filters 1-4, Cincinnati, Ohio Study

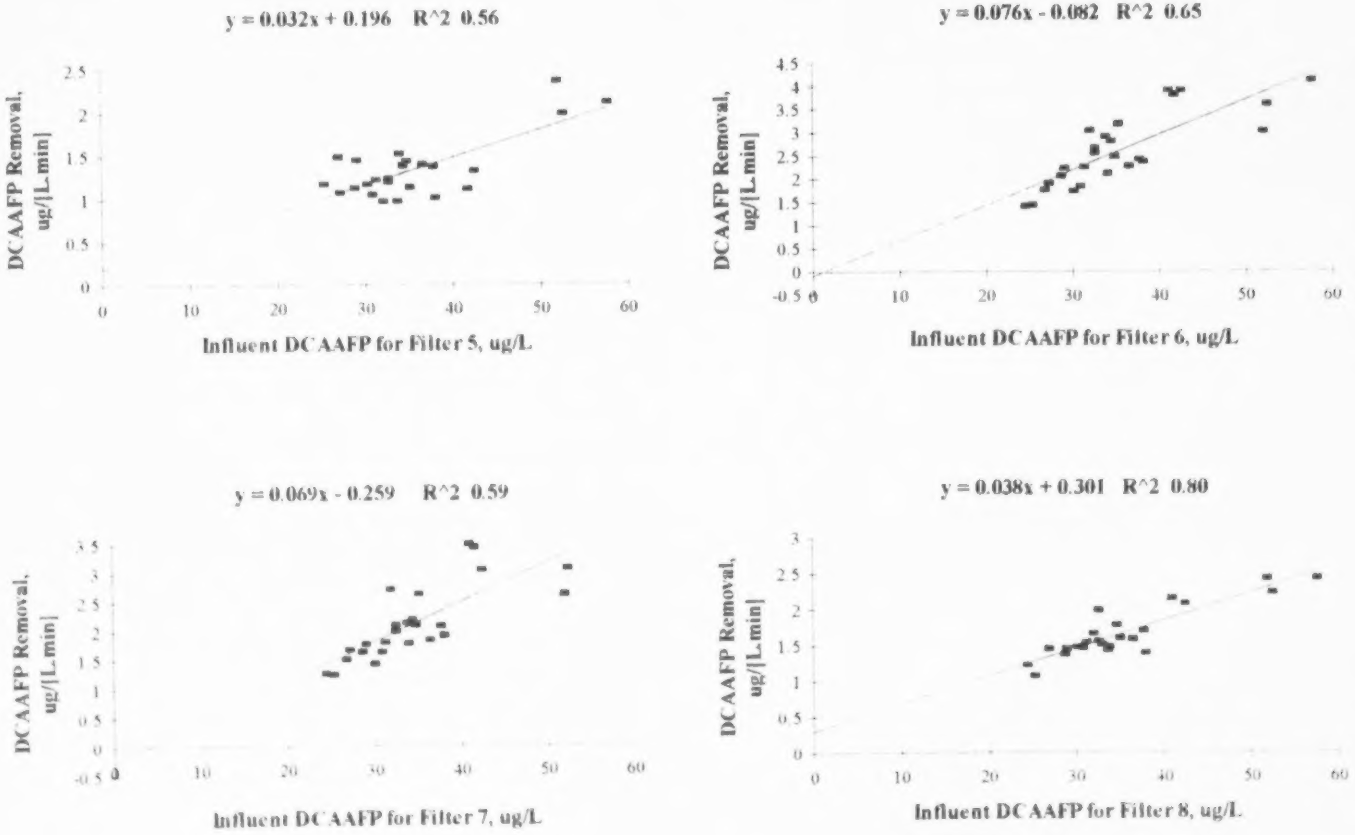


Figure B19 DCAAFP Removal Rate vs. Influent Concentration for Filters 5-8, Cincinnati, Ohio Study

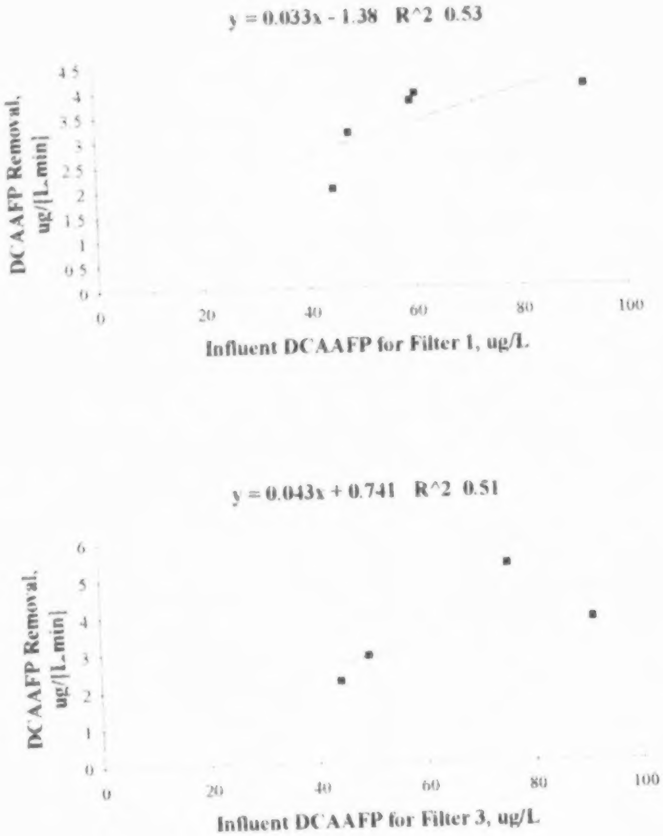


Figure B20: DCAAFP Removal Rate vs Influent Concentration for Filters 1 and 3, Woodbridge, CT Study

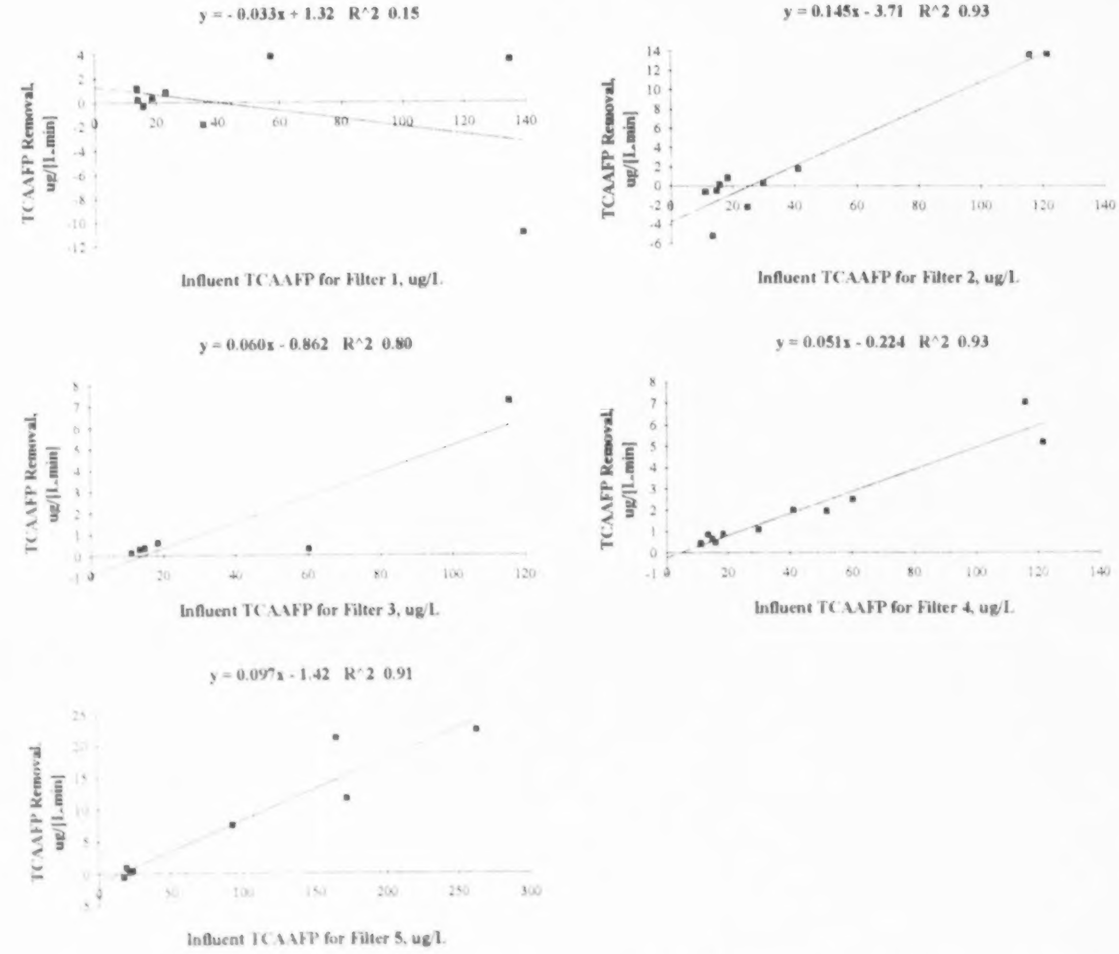


Figure 21 TCAAFP Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta, 1992-1993 Study

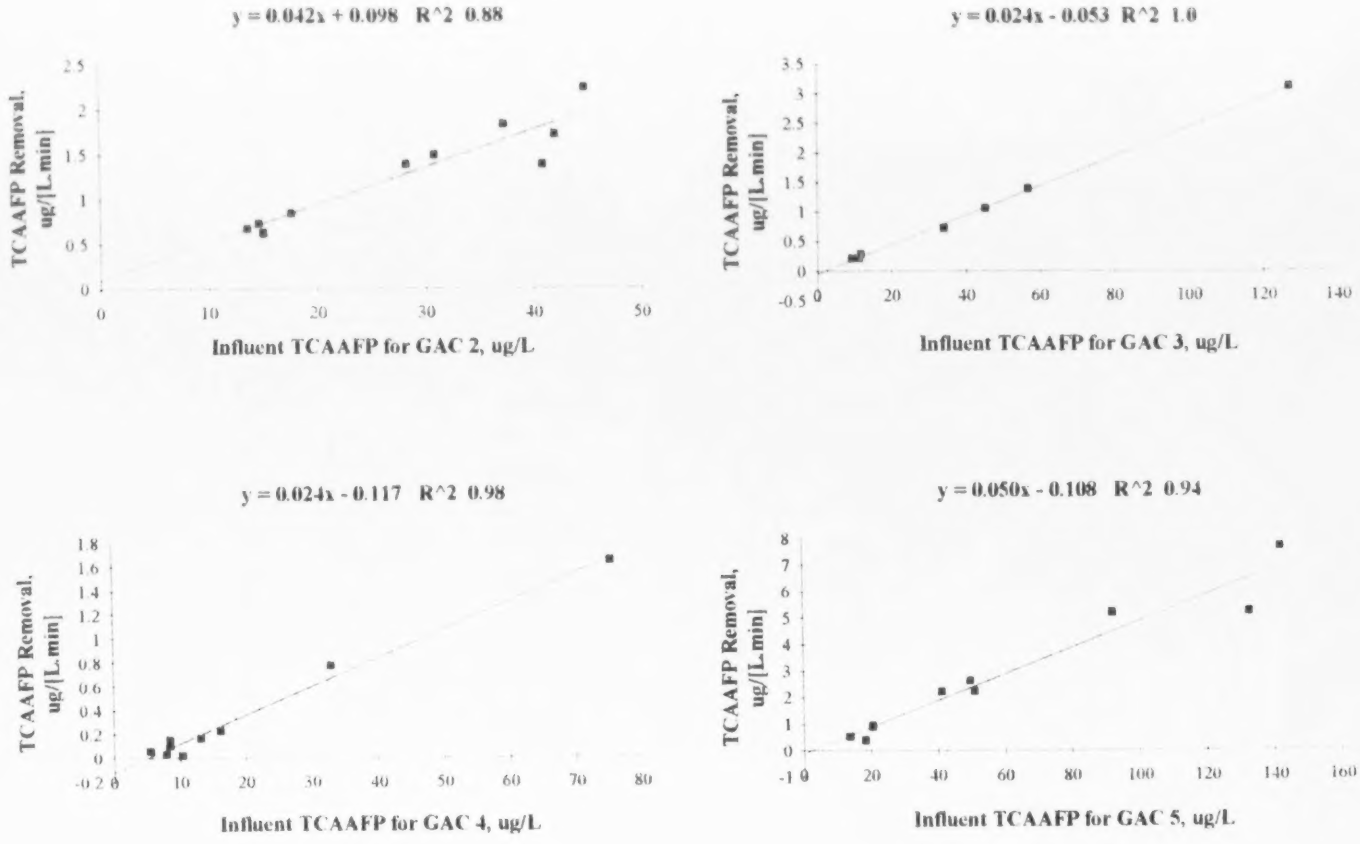


Figure B22: TCAAFP Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta, 1992-1993 Study

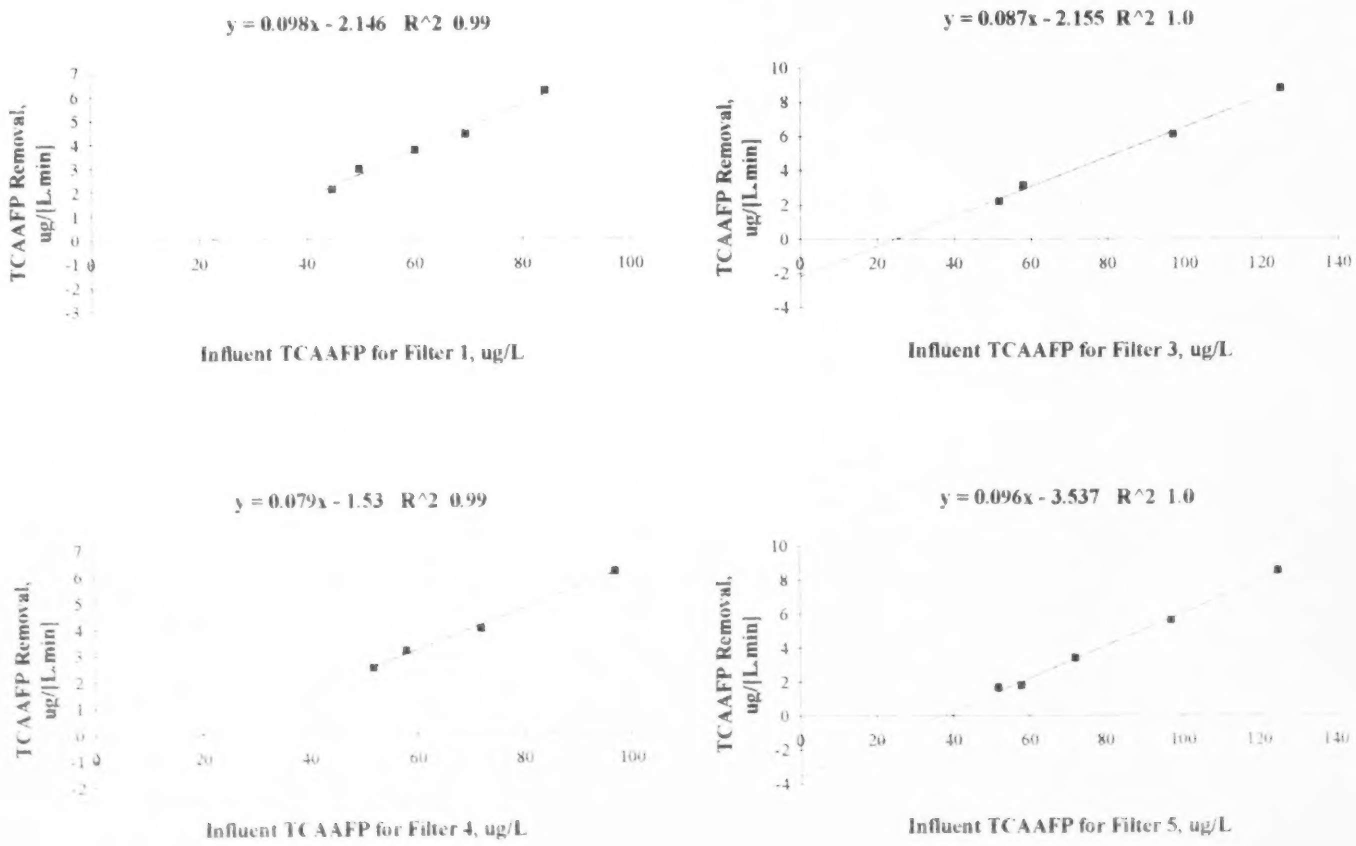


Figure B23 TCAAFP Removal Rate vs. Influent Concentration for Filters, Woodbridge, CT Study

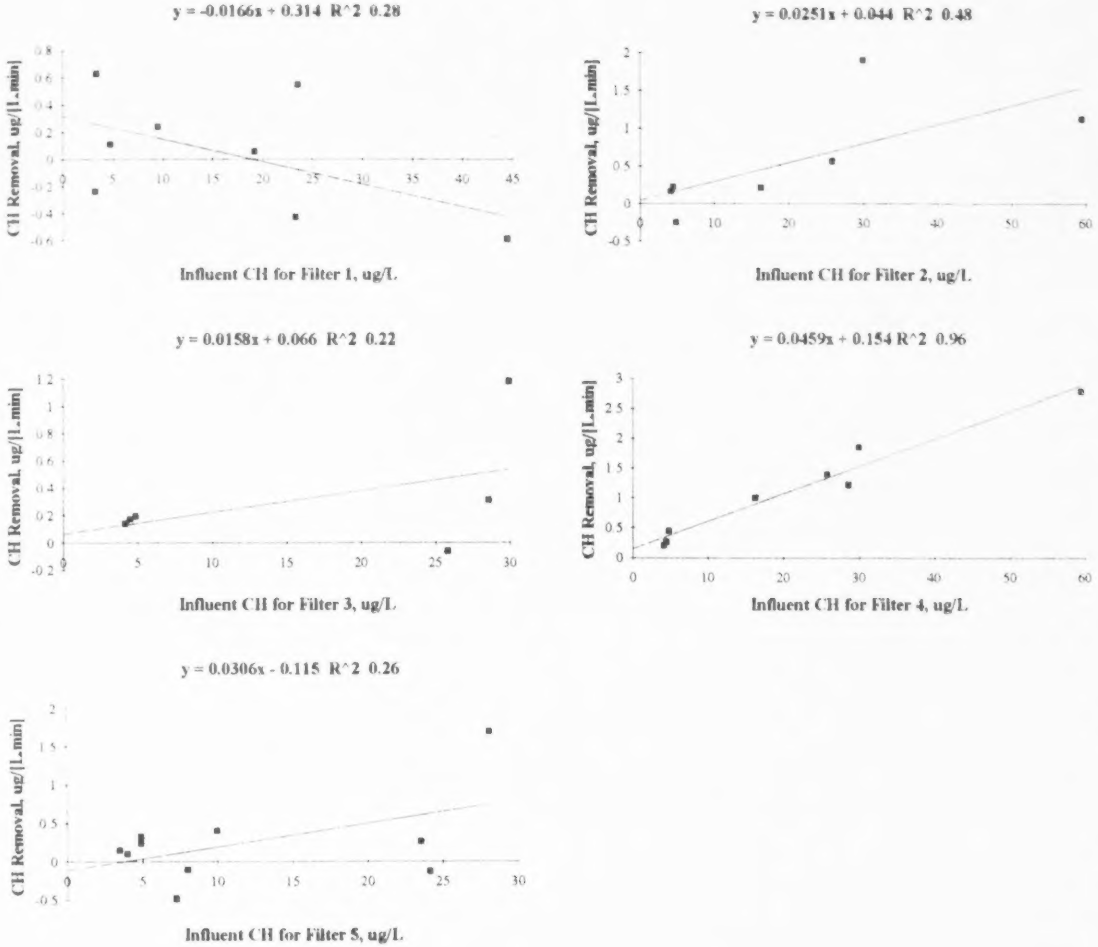


Figure B24: Chloral Hydrate FP Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

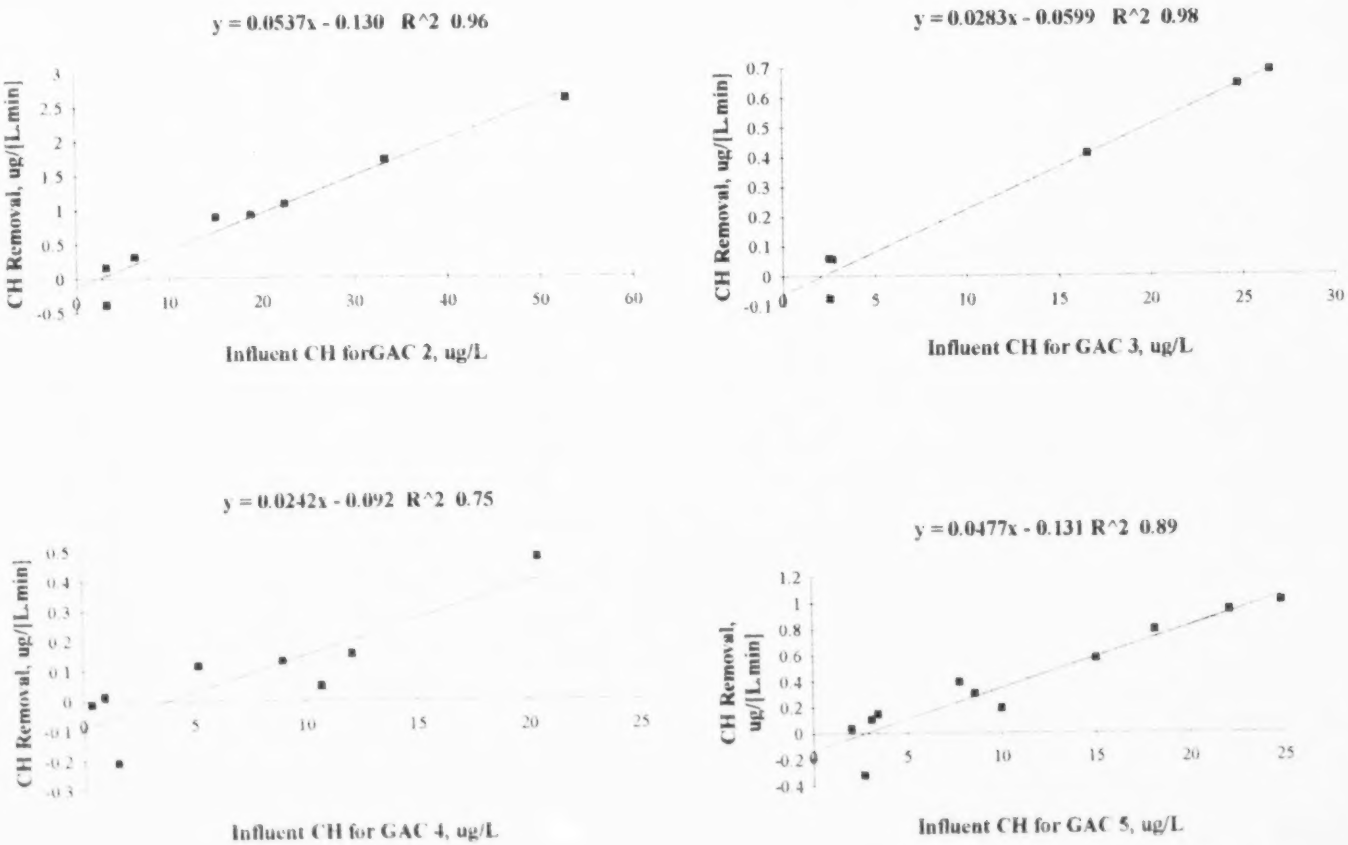


Figure B25. Chloral Hydrate Formation Potential Removal Rata vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

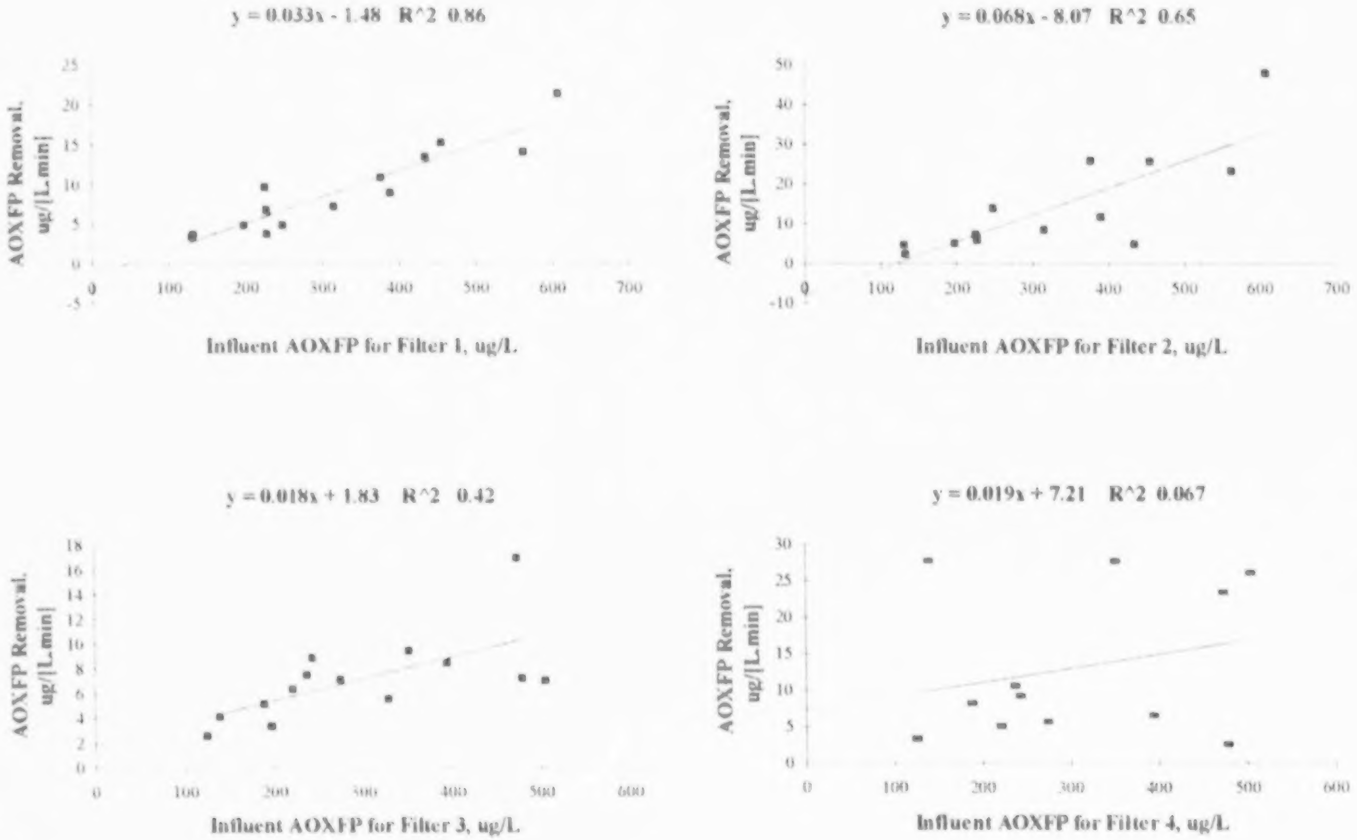


Figure B26 AOXFP Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1989-1990 Study

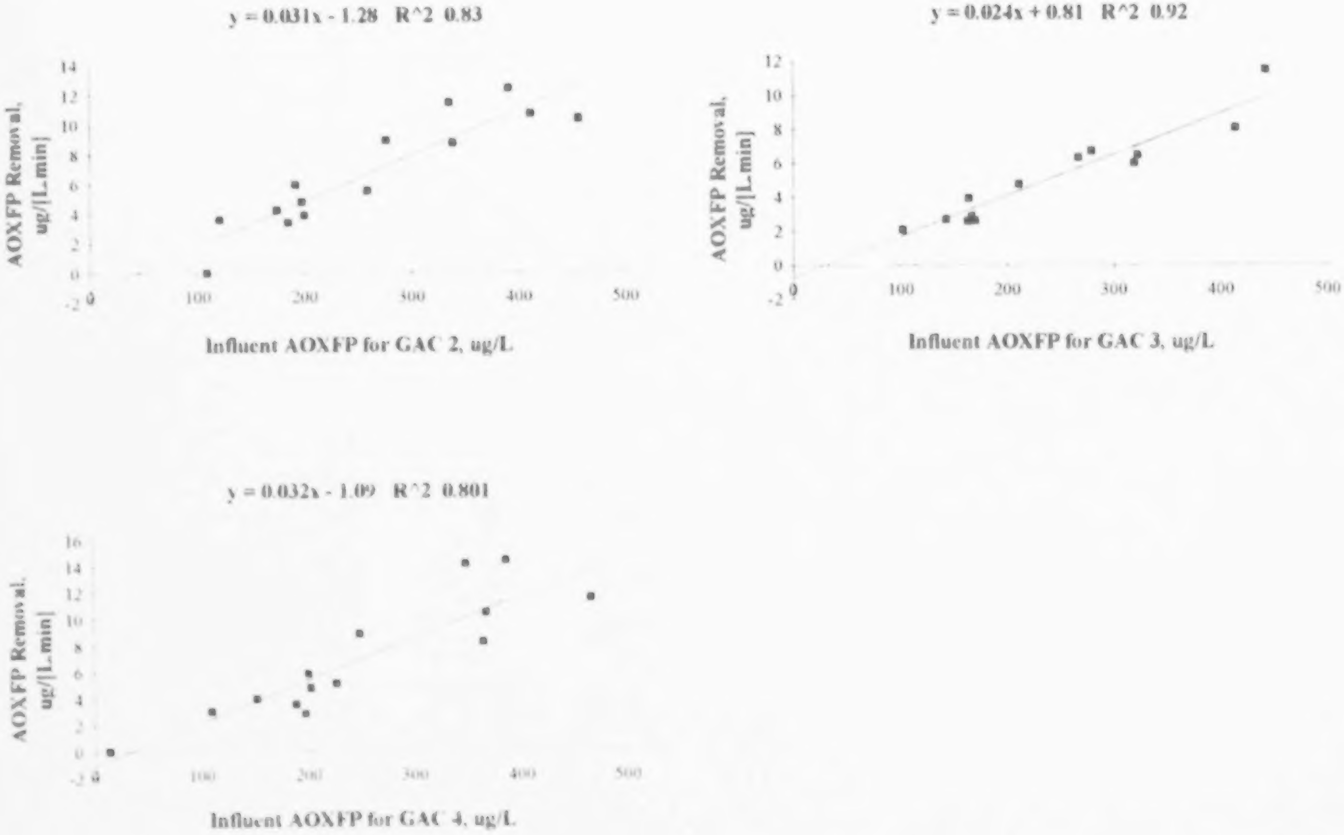


Figure B27 AOXFP Removal Rate vs Influent Concentration for GAC Contactors, Edmonton, Alberta 1989-1990 Study

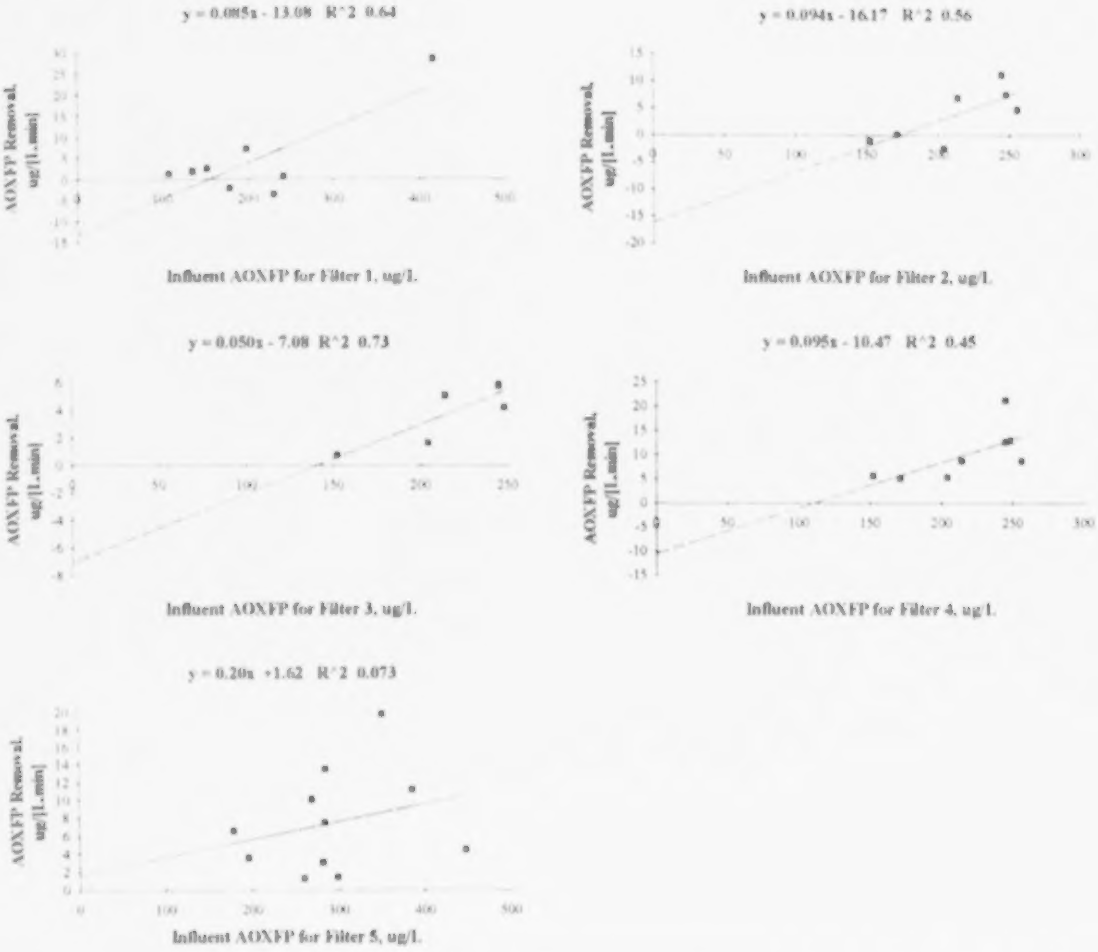


Figure B28 AOXFP Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

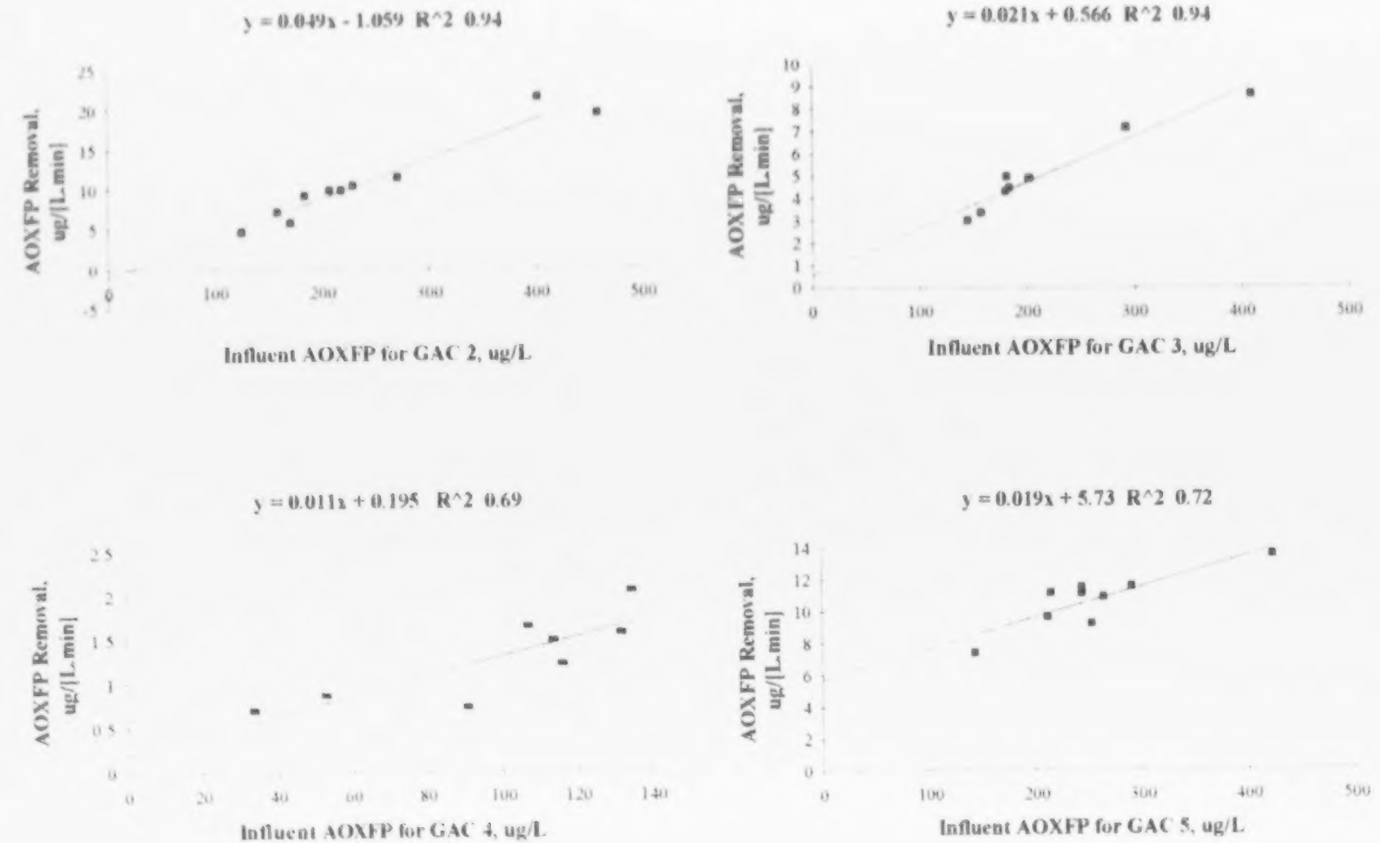


Figure B29 AOXFP Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

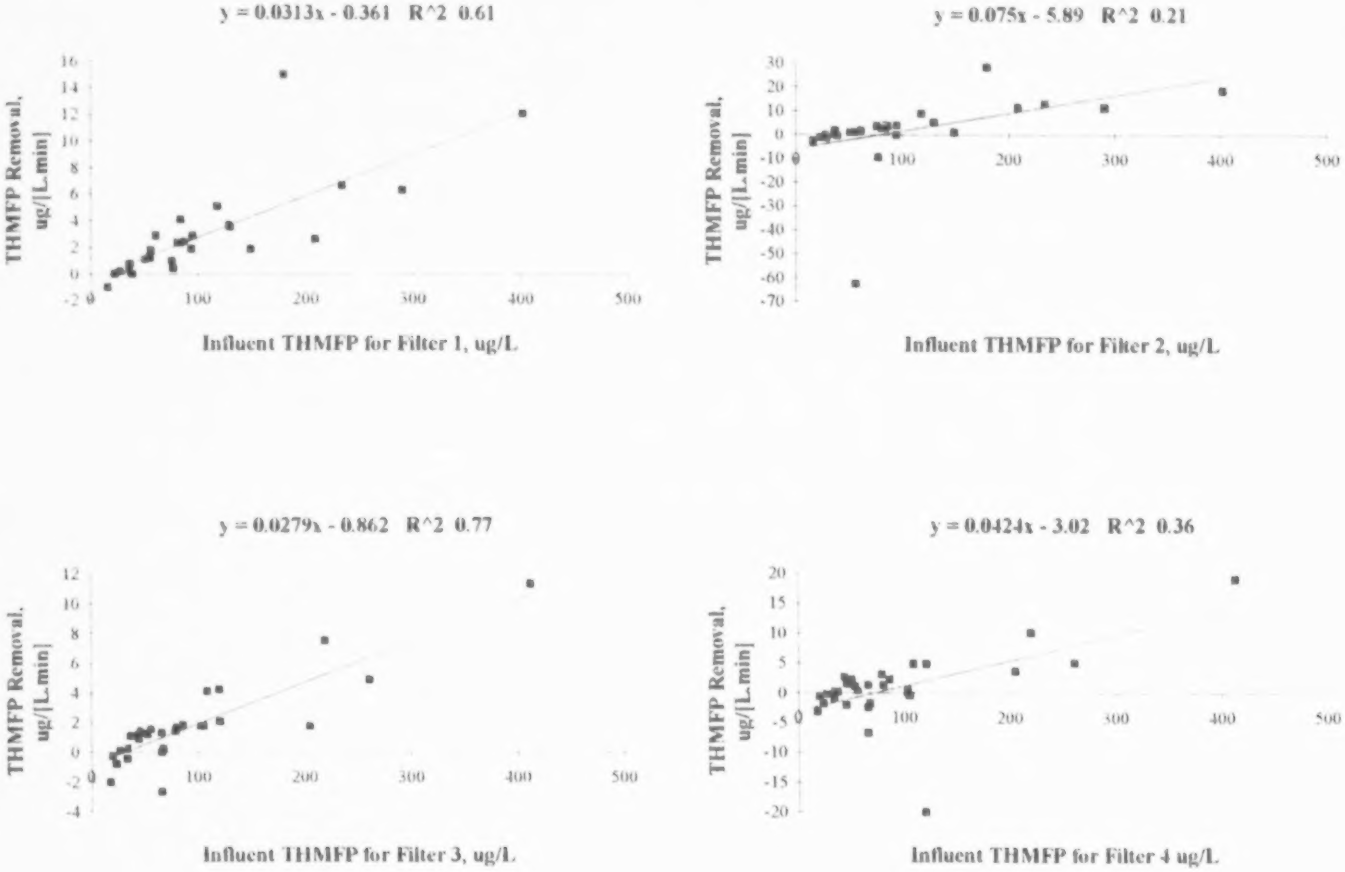


Figure B30 THMFP Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1989-1990 Study

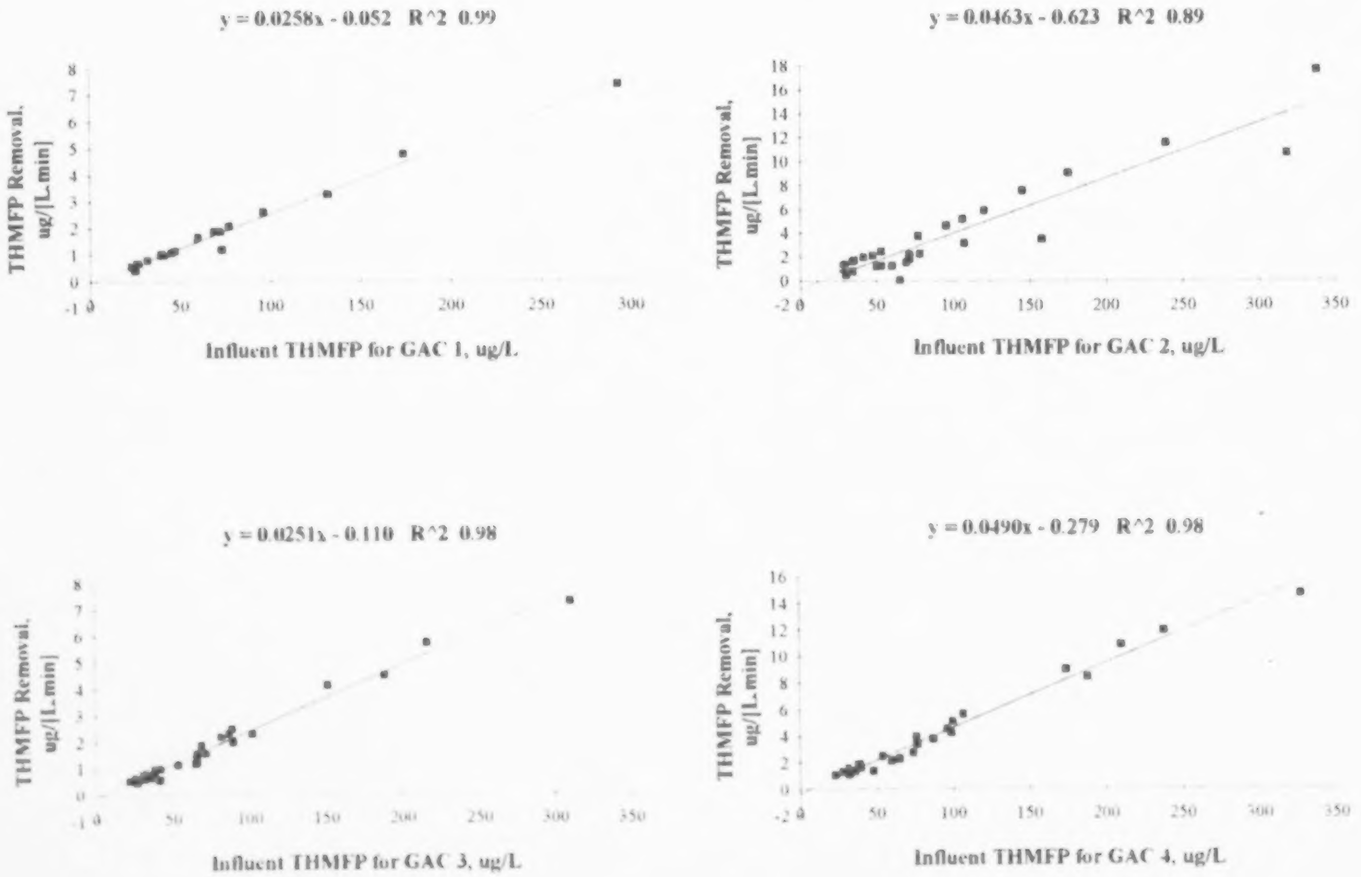
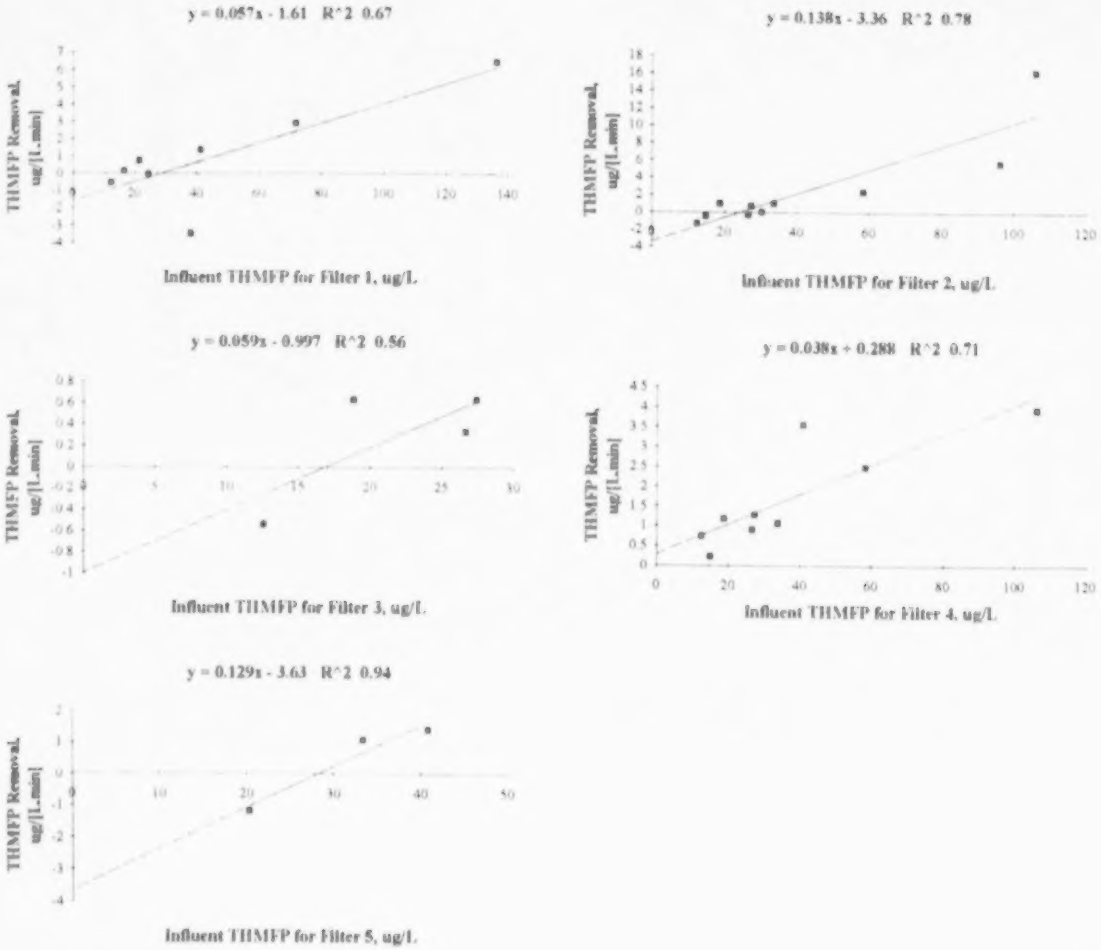


Figure B31 THMFP Removal Rate vs Influent Concentration for GAC Contactors, Edmonton, Alberta 1989-1990 Study



y = 0.057x - 1.61 R^2 0.67

y = 0.138x - 3.36 R^2 0.78

y = 0.059x - 0.997 R^2 0.56

y = 0.038x + 0.288 R^2 0.71

y = 0.129x - 3.63 R^2 0.94

Figure B32 THMFP Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

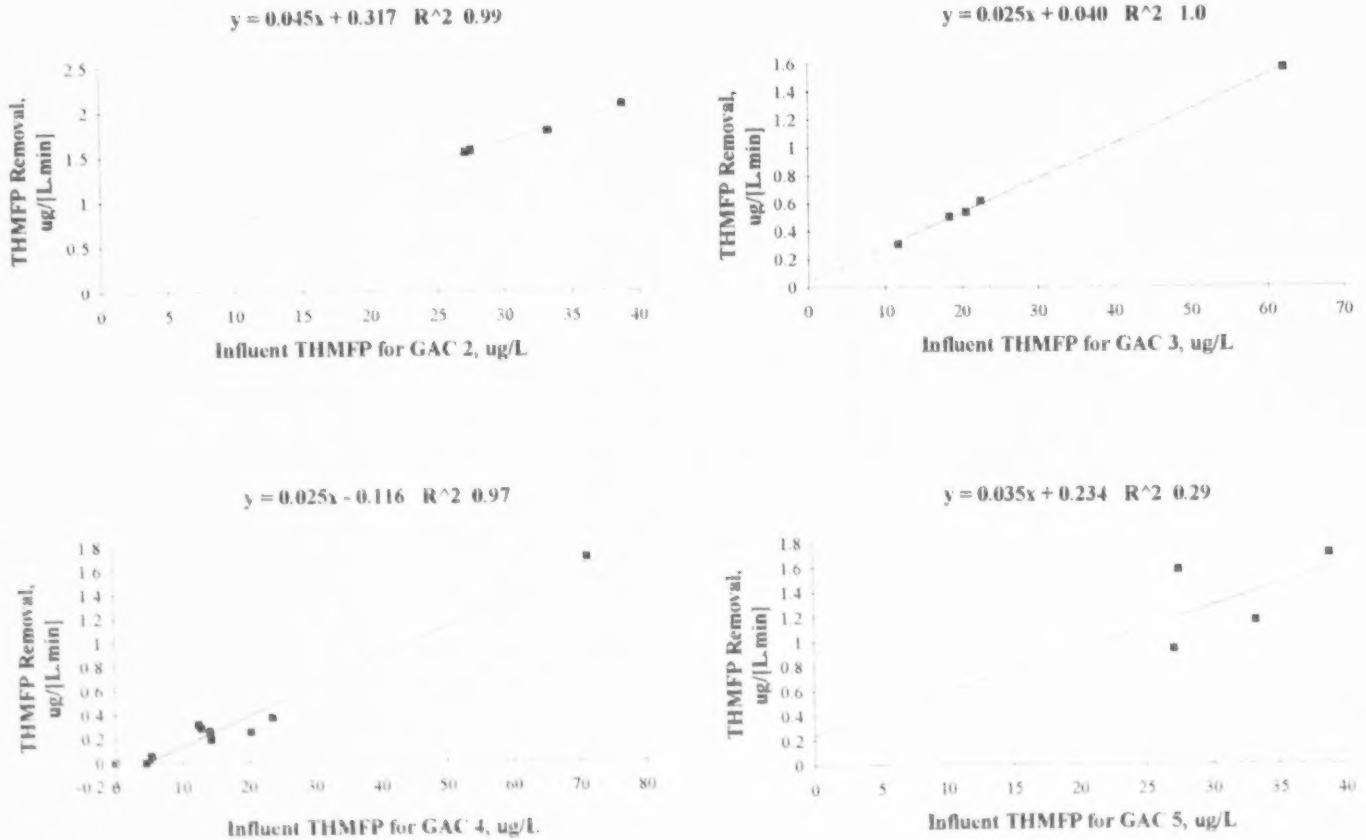


Figure B33 THMFP Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

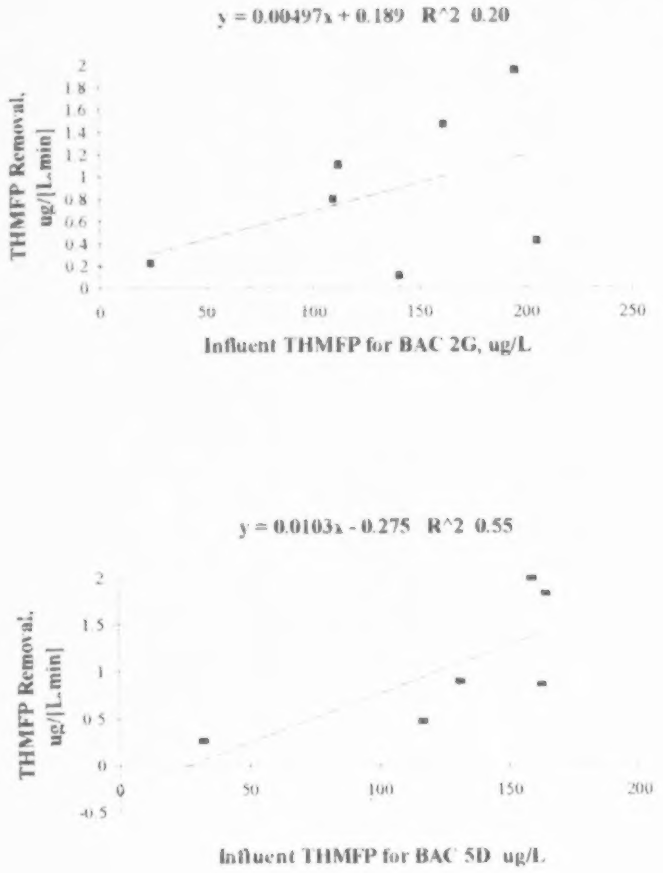


Figure B34: THMFP Removal Rate vs Influent Concentration for BAC Contactors, Laval, Quebec Study

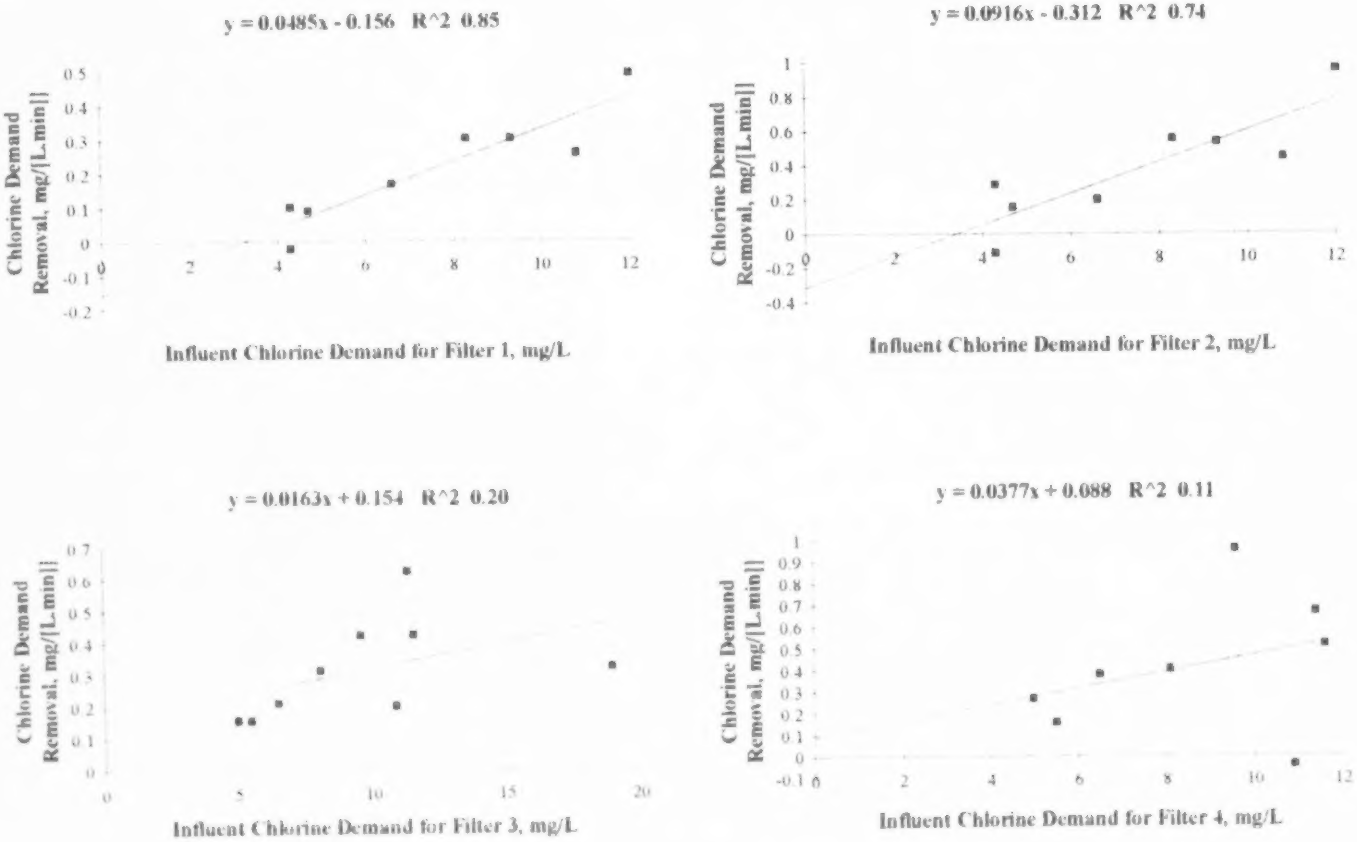


Figure B35 Chlorine Demand Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta 1989-1990 Study

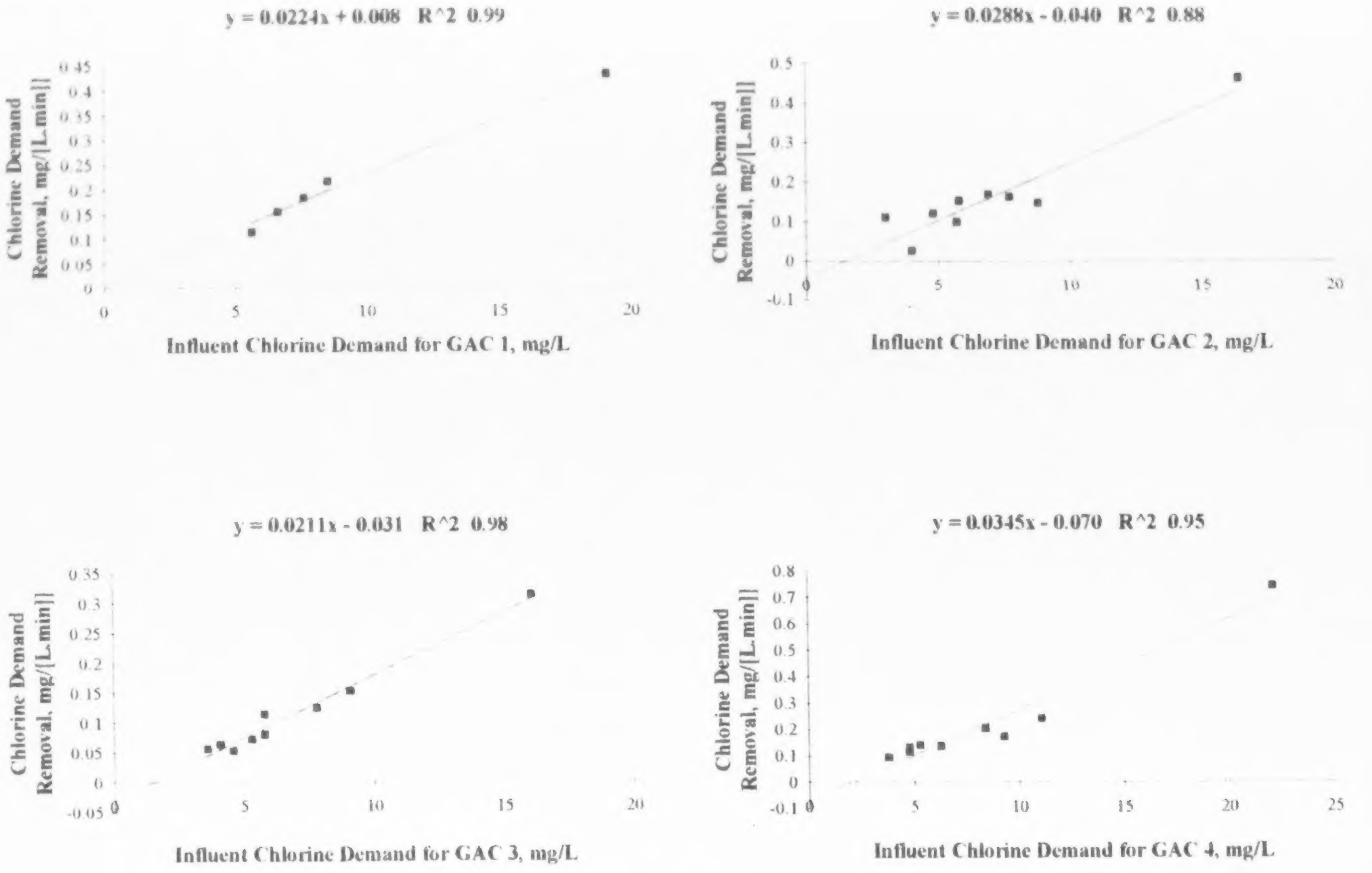


Figure B36: Chlorine Demand Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1989-1990 Study

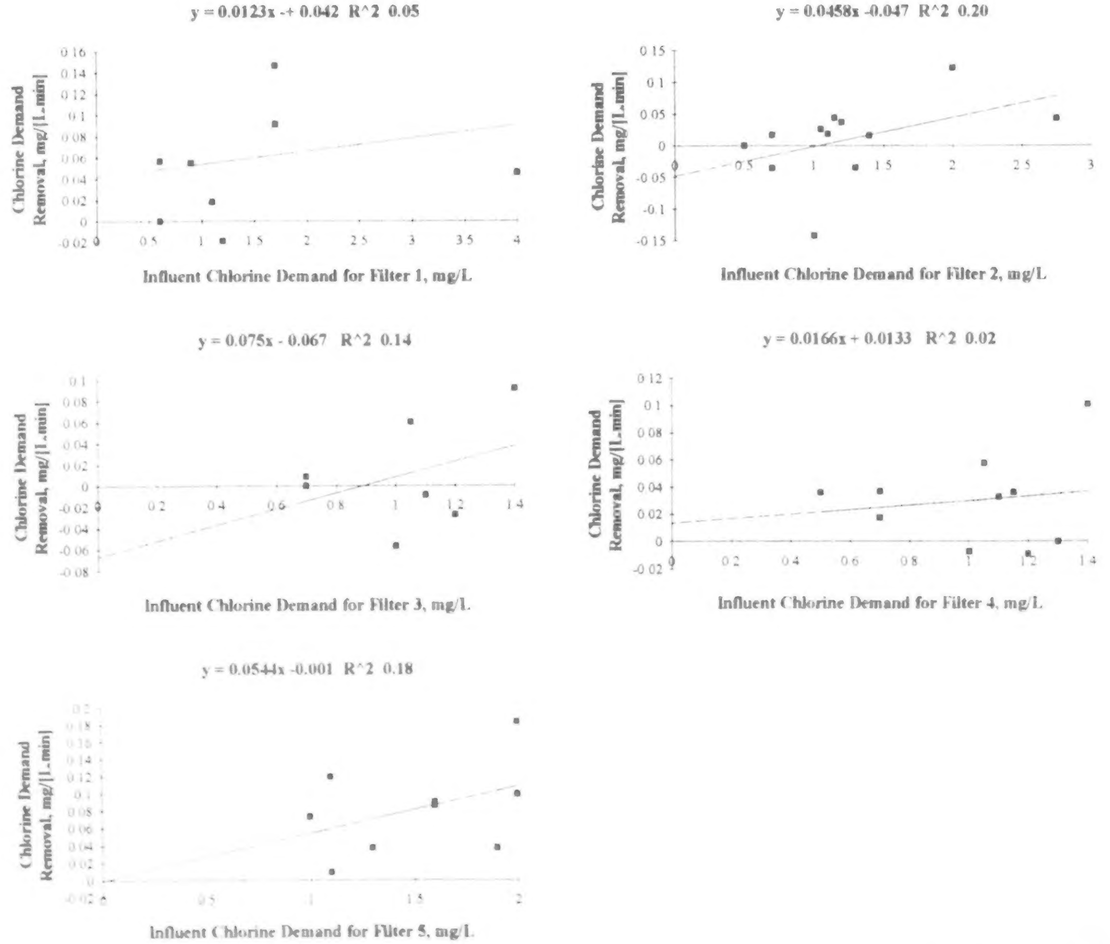


Figure B37 Chlorine Demand Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta 1992-1993

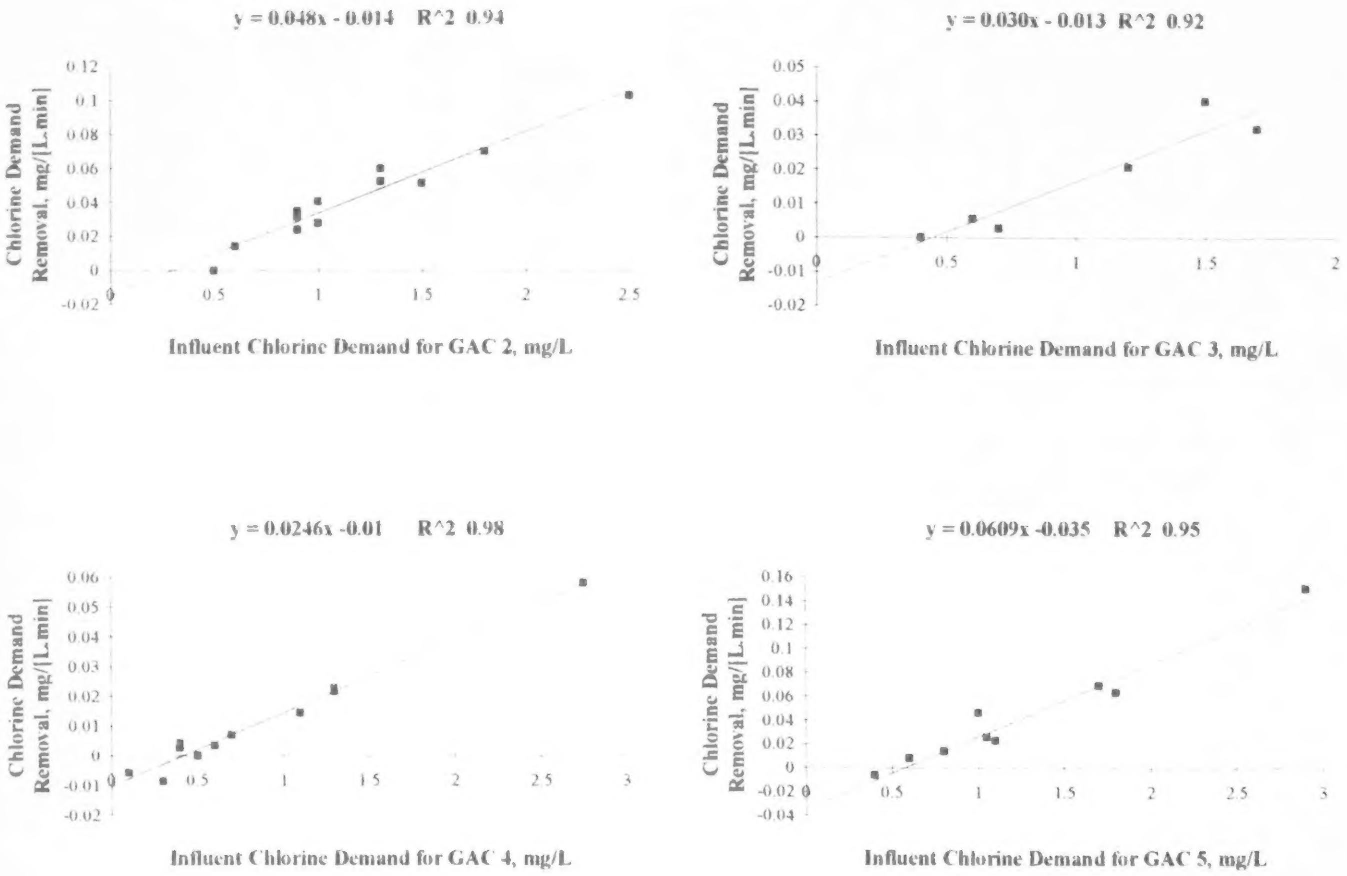


Figure B38: Chlorine Demand Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

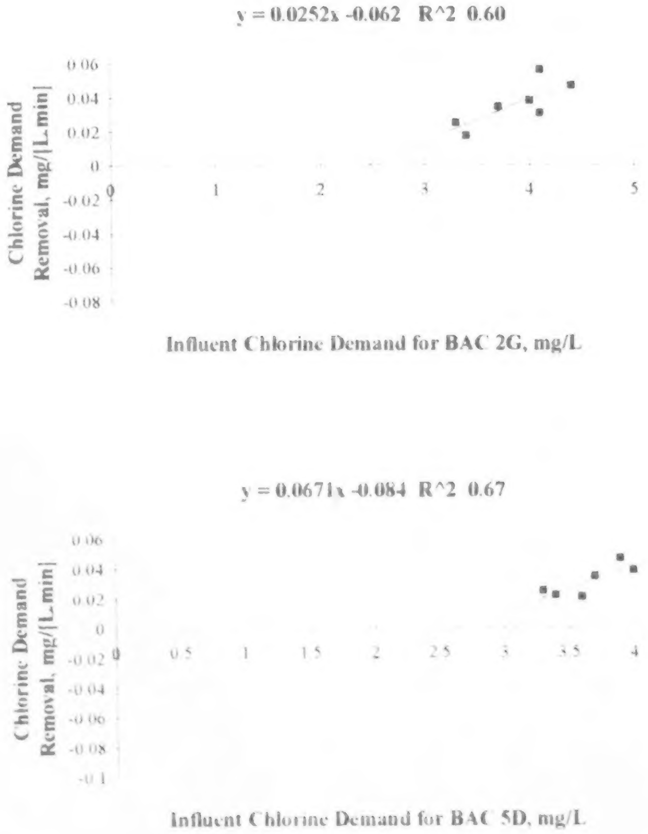


Figure B39 Chlorine Demand Removal Rate vs. Influent Concentration for BAC Contactors for Laval, Quebec Study

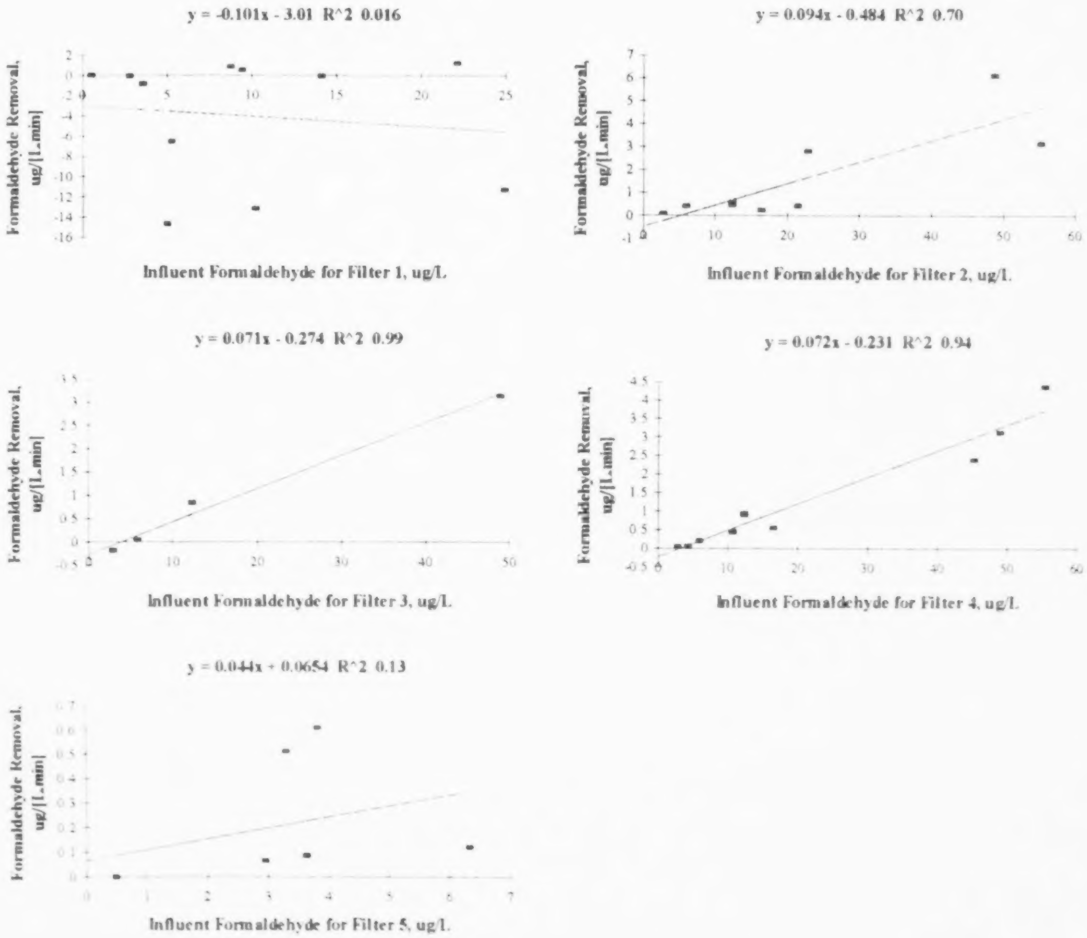


Figure B41 Formaldehyde Removal Rate vs Influent Concentration for Filters Edmonton, Alberta Study 1992-1993 Study

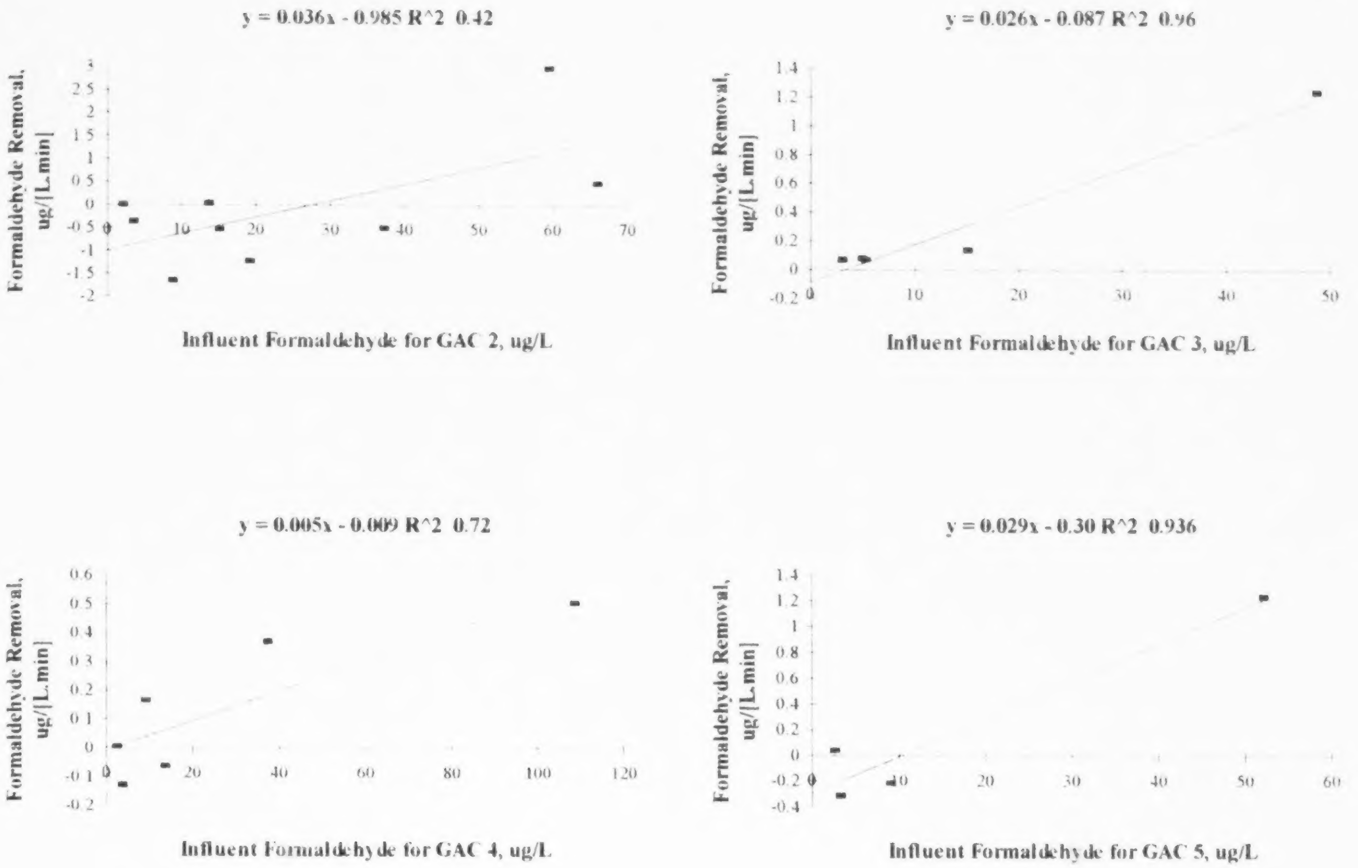


Figure B42: Formaldehyde Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993

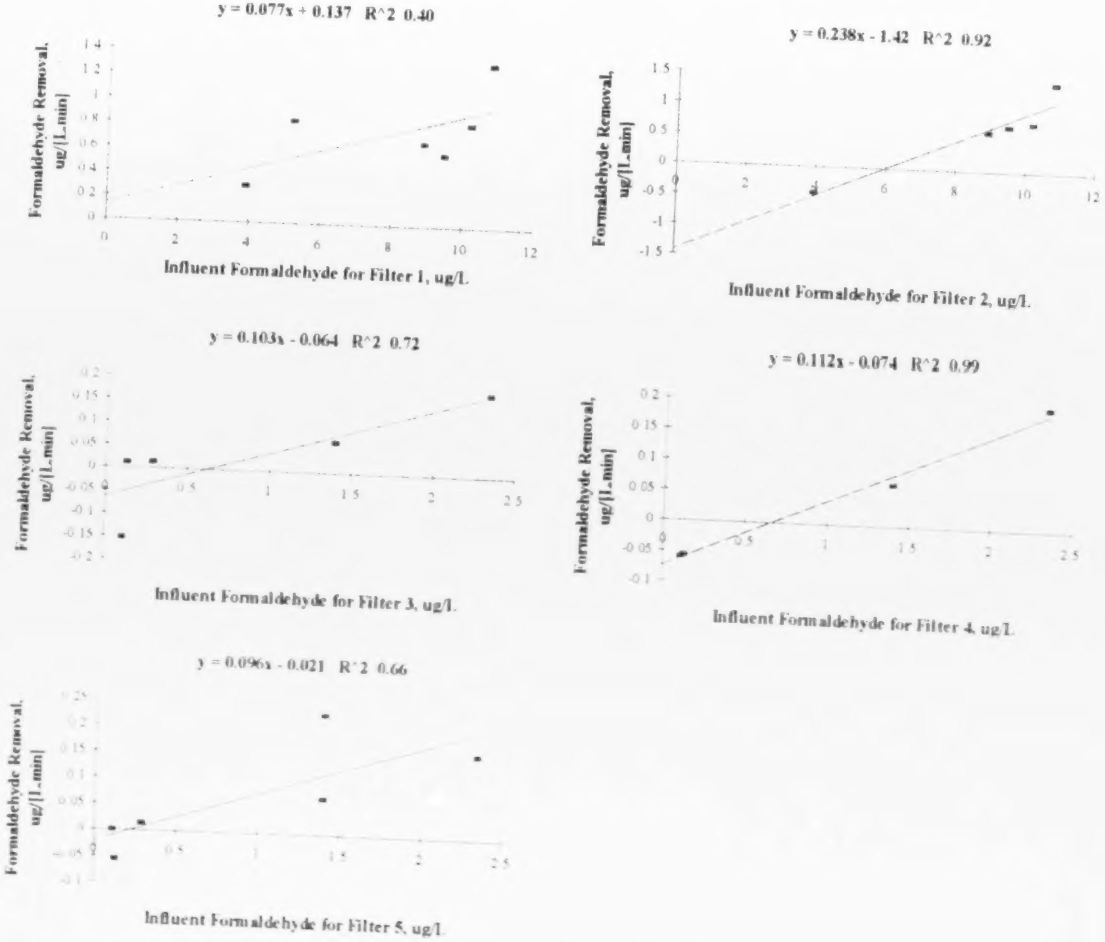


Figure B43 Formaldehyde Removal Rate vs Influent Concentration for Filters Woodbridge, CT Study

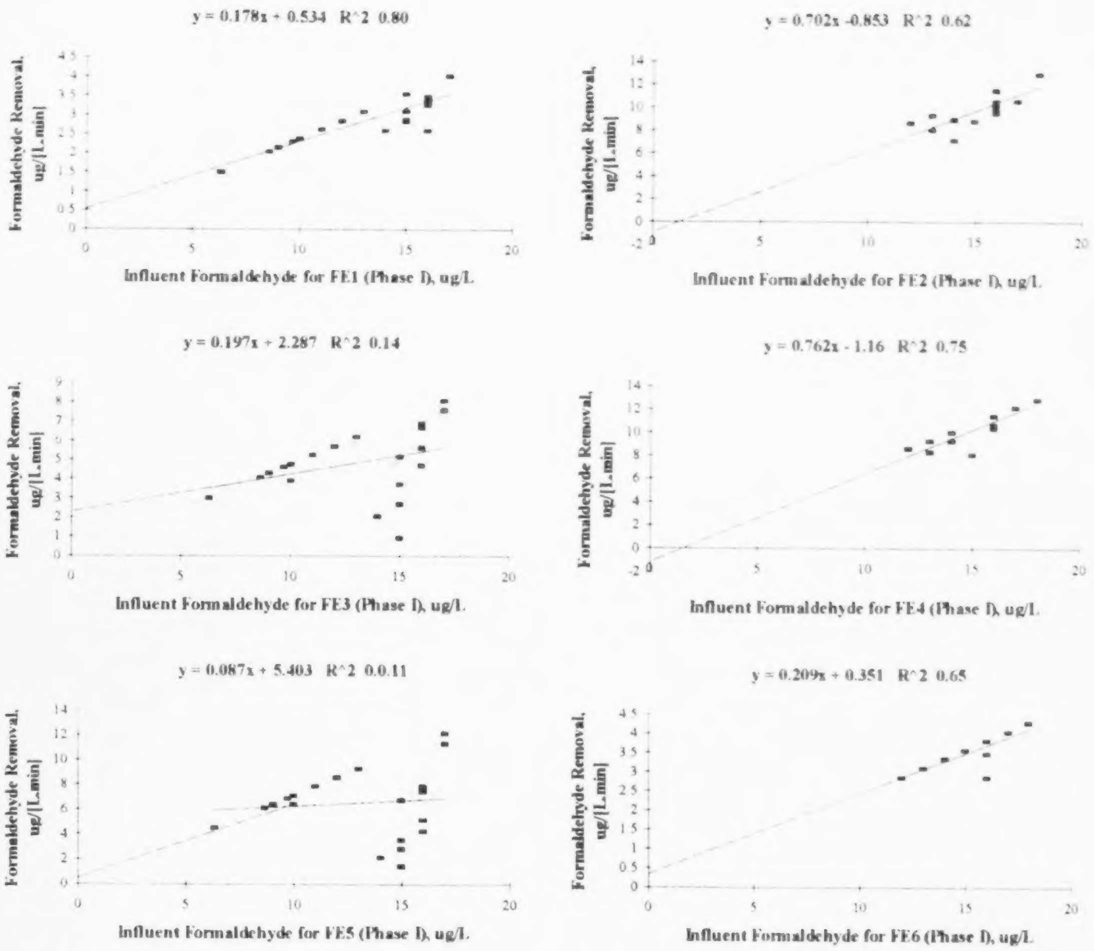


Figure B44: Formaldehyde Removal vs. Influent Concentration for Filter (Phase I), Southern California Study

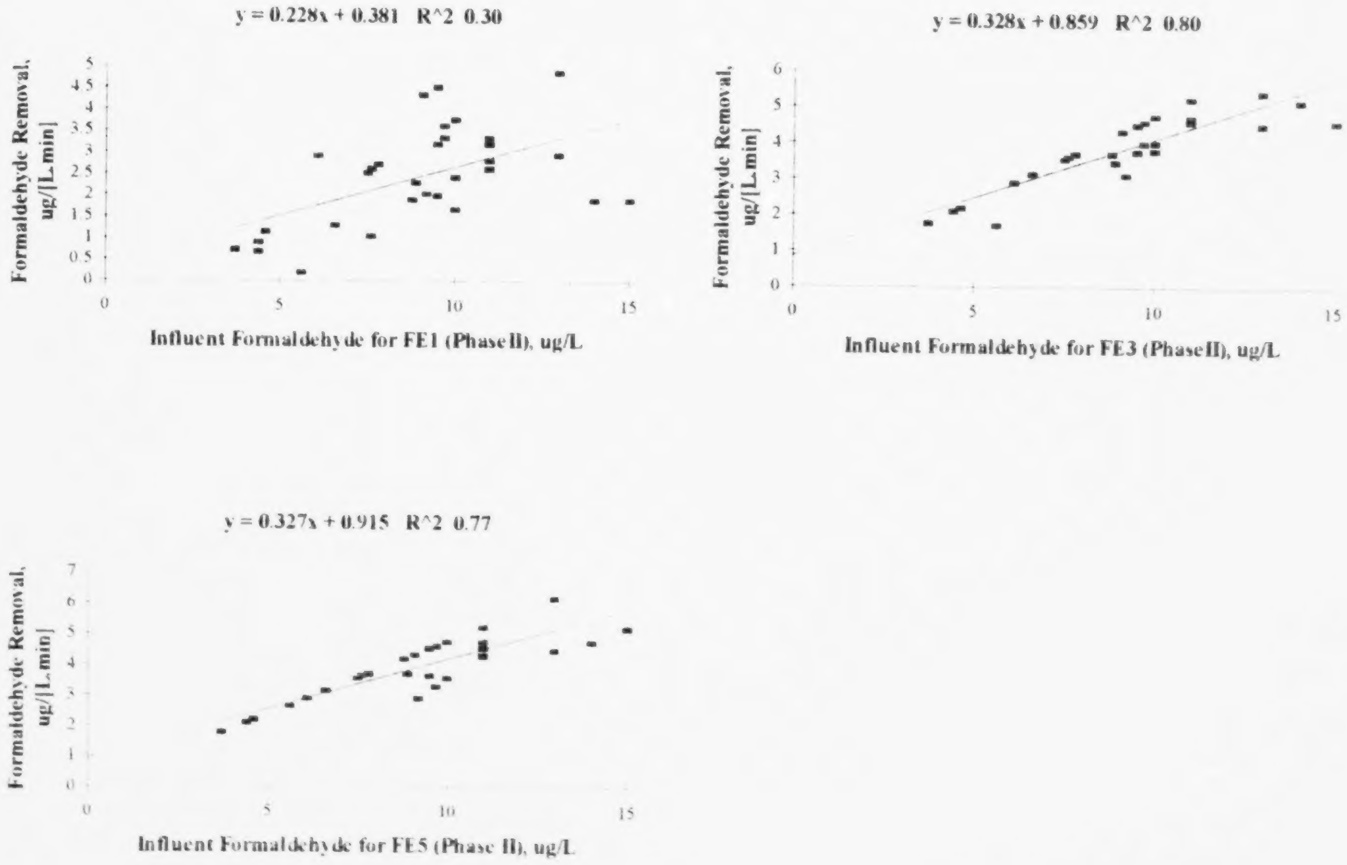


Figure B45 Formaldehyde Removal Rate vs Influent Concentration for Filters (Phase II), Southern California Study

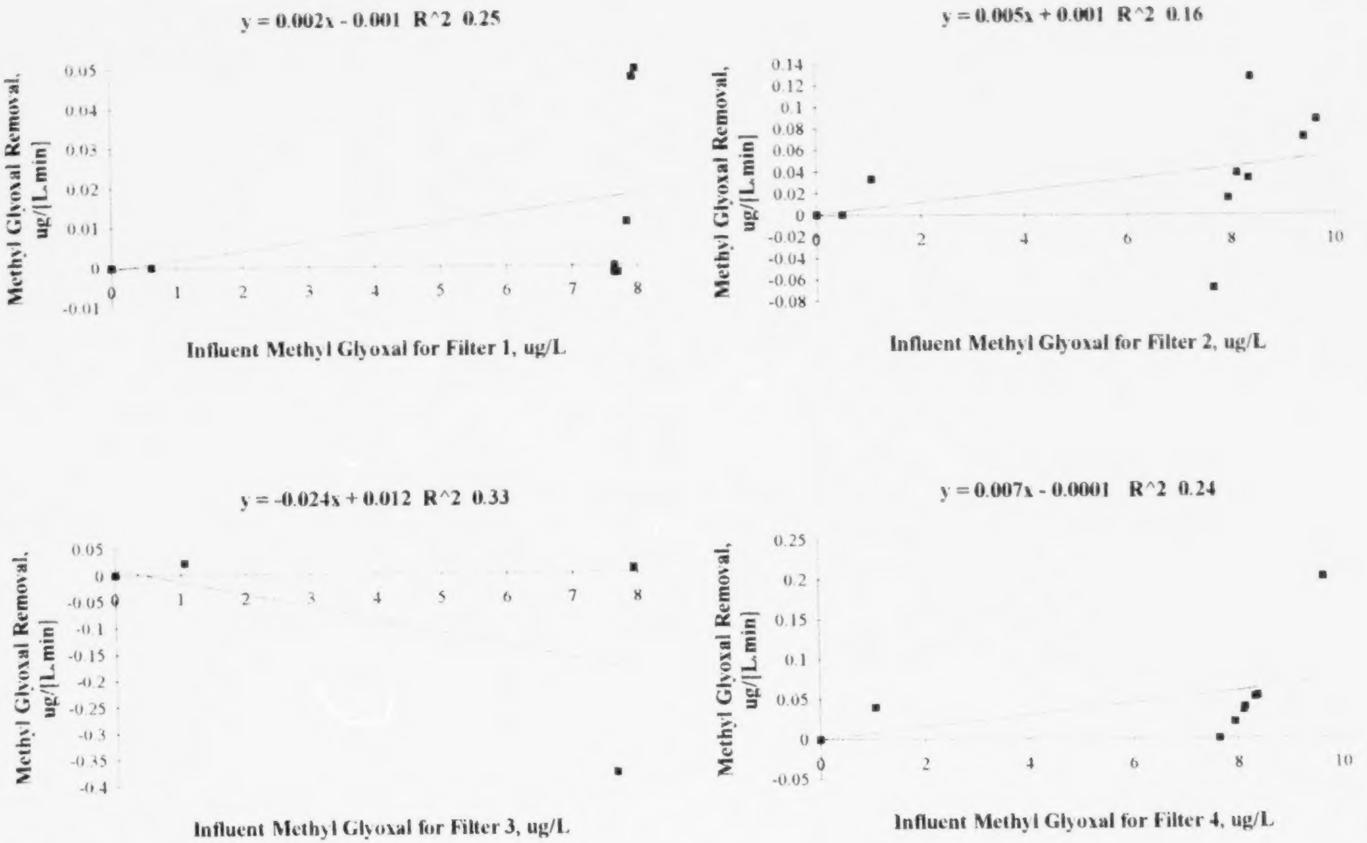


Figure B46: Methyl Glyoxal Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

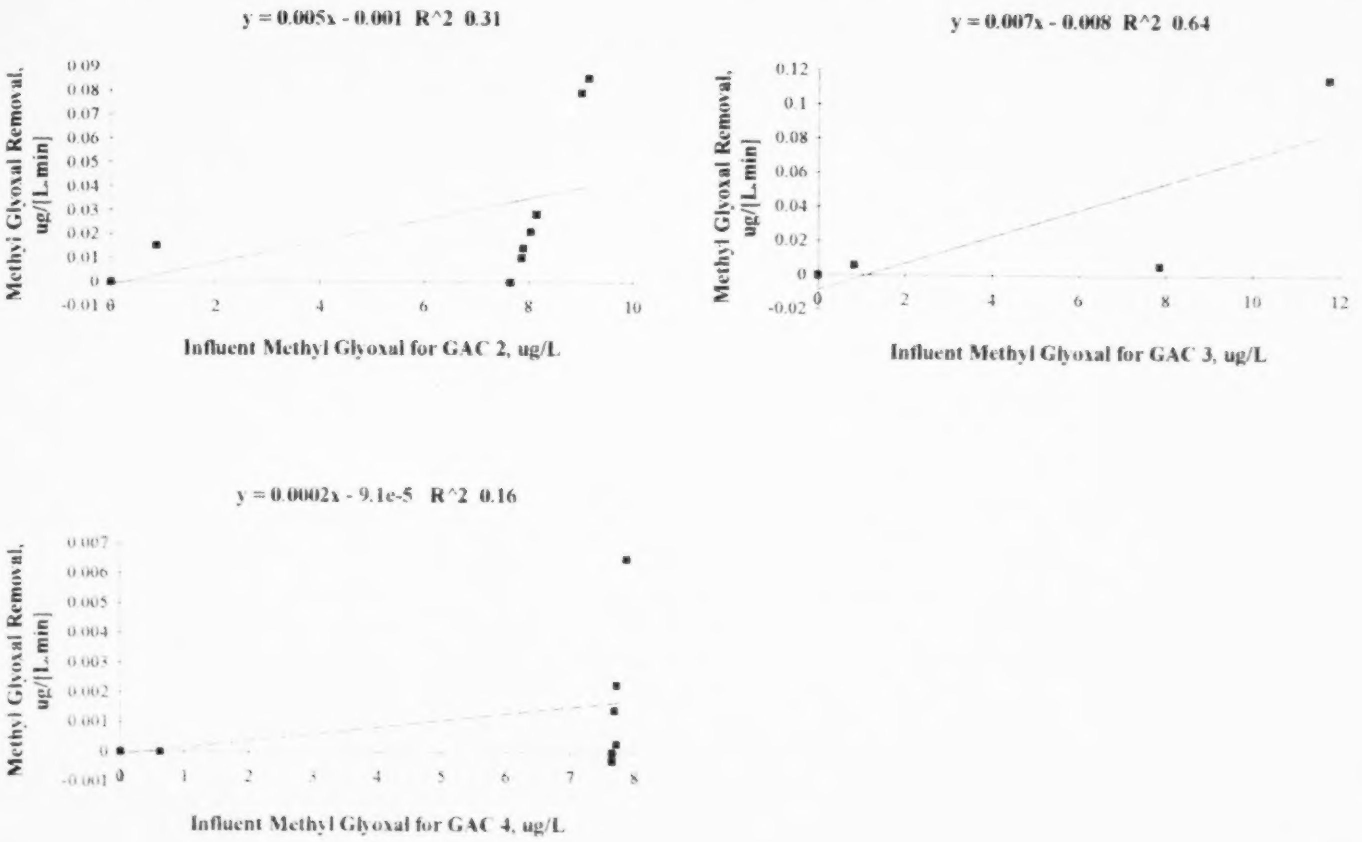


Figure B47 Methyl Glyoxal Removal Rate vs Influent Concentration for GAC Contactors for Edmonton, Alberta 1992-1993 Study

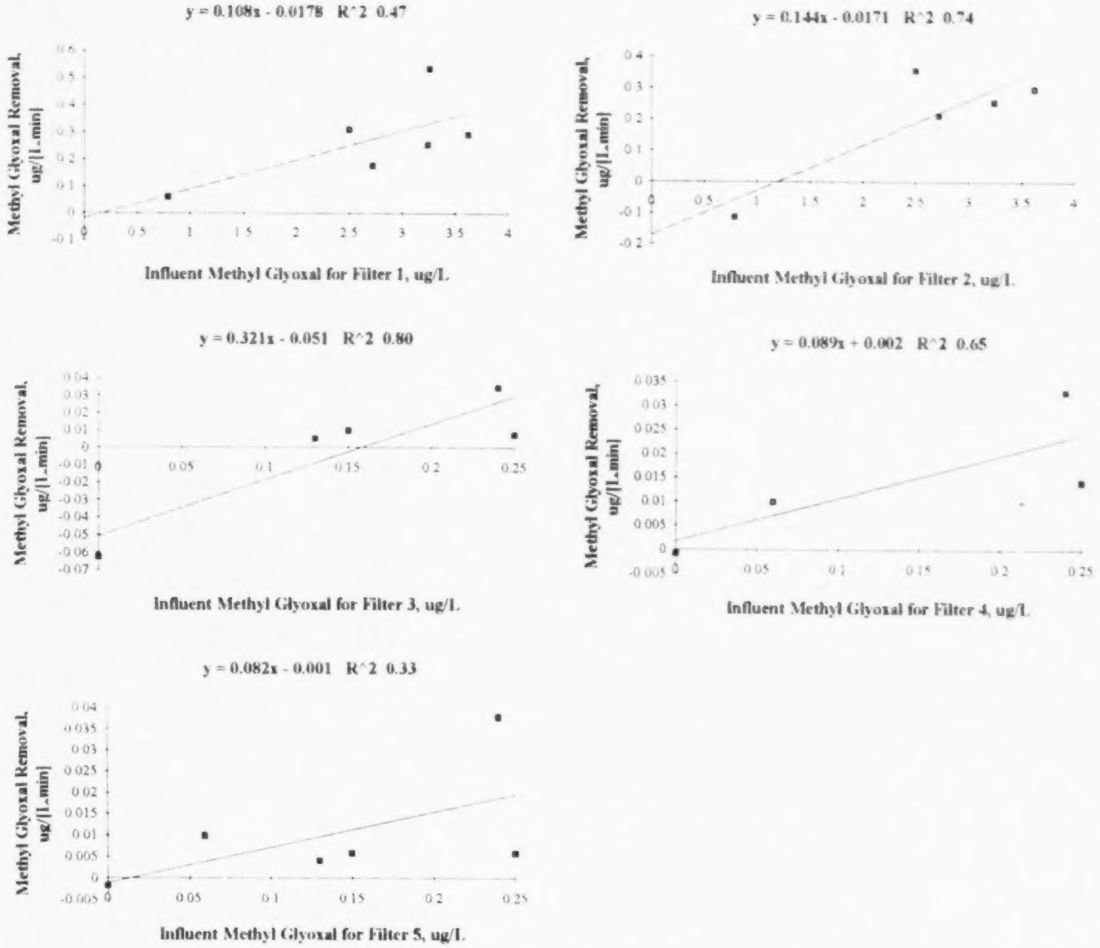


Figure B48 Methyl Glyoxal Removal Rate vs Influent Concentration for Filters, Woodbridge, CT Study

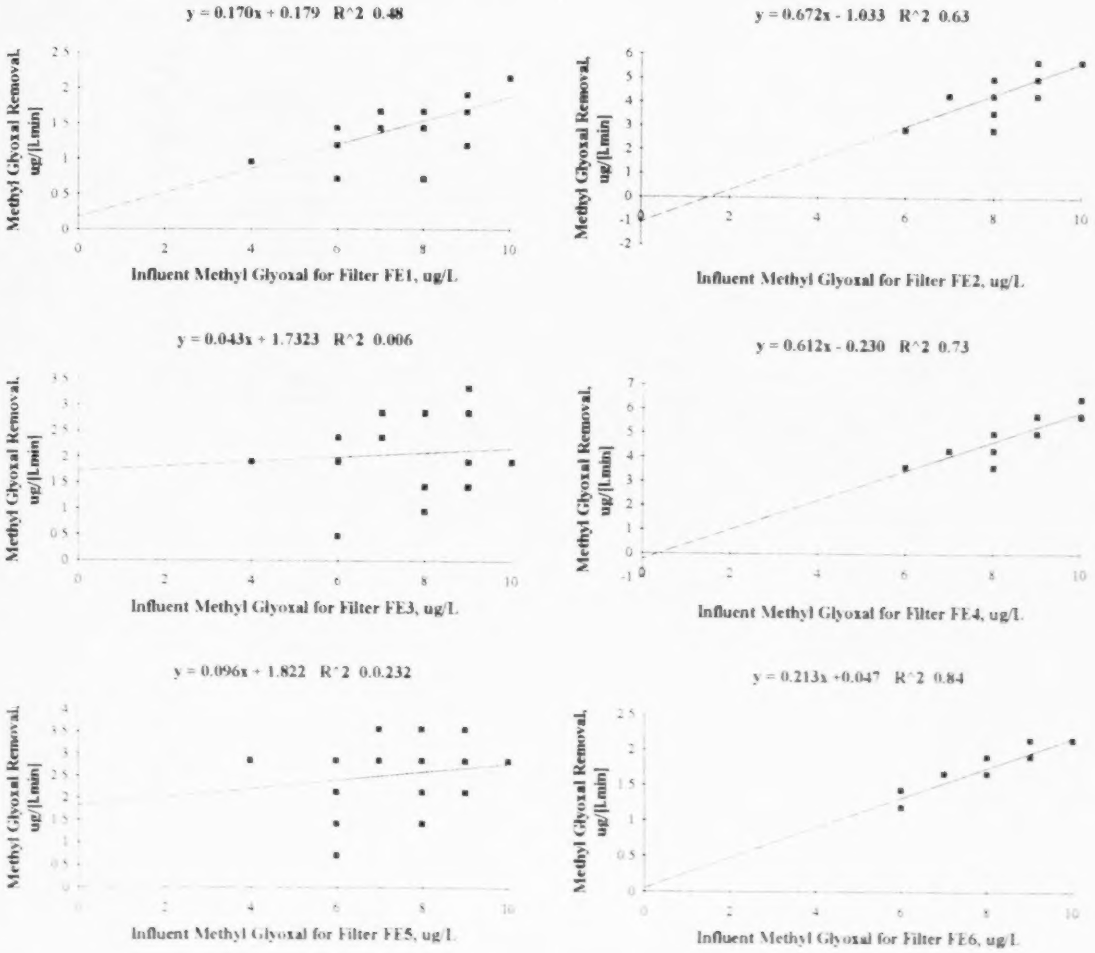


Figure B49 Methyl Glyoxal Removal Rate vs Influent Concentration for Filter (Phase I) Southern California Study

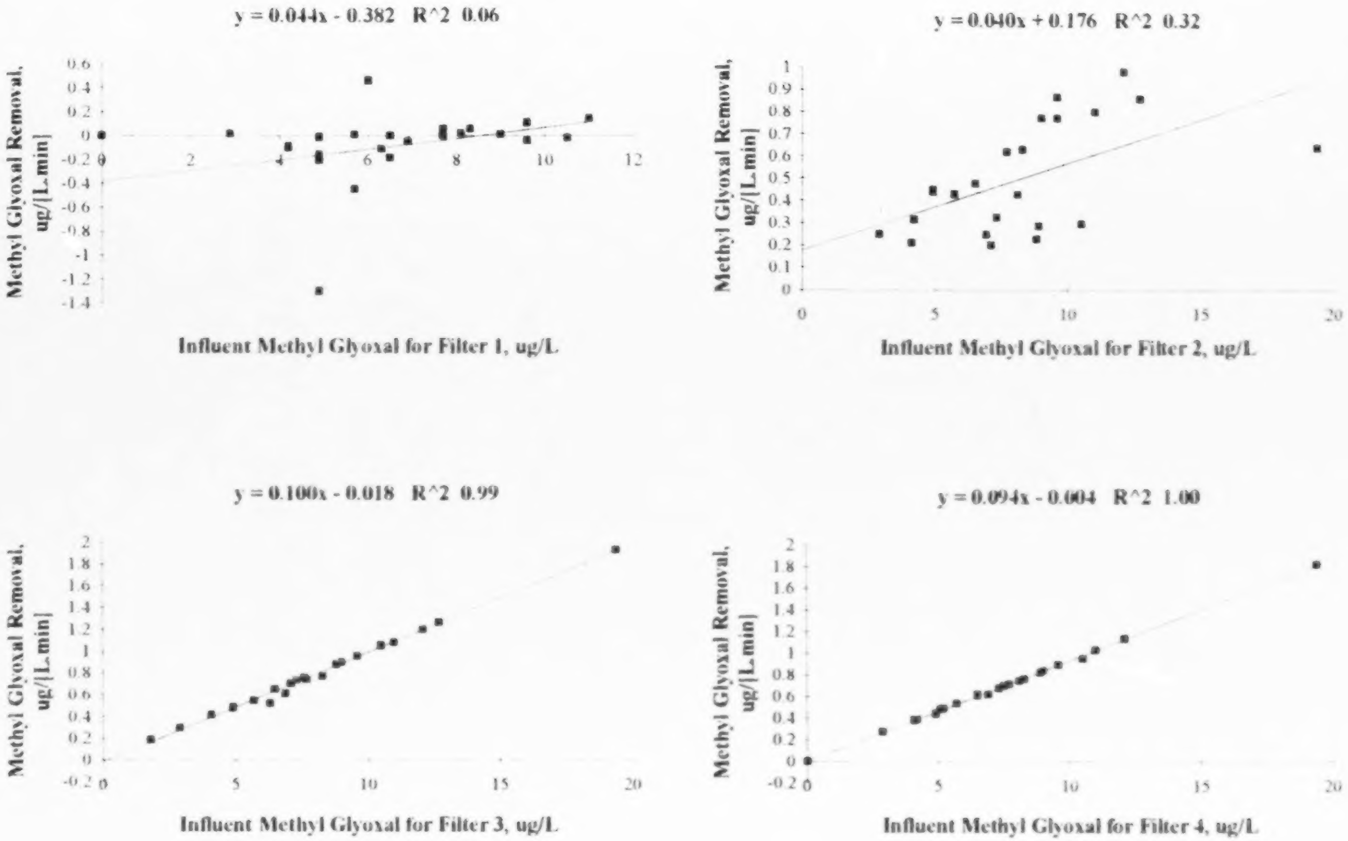


Figure B50 Methyl Glyoxal Removal Rate vs. Influent Concentration for Filters 1-4, Cincinnati, Ohio Study

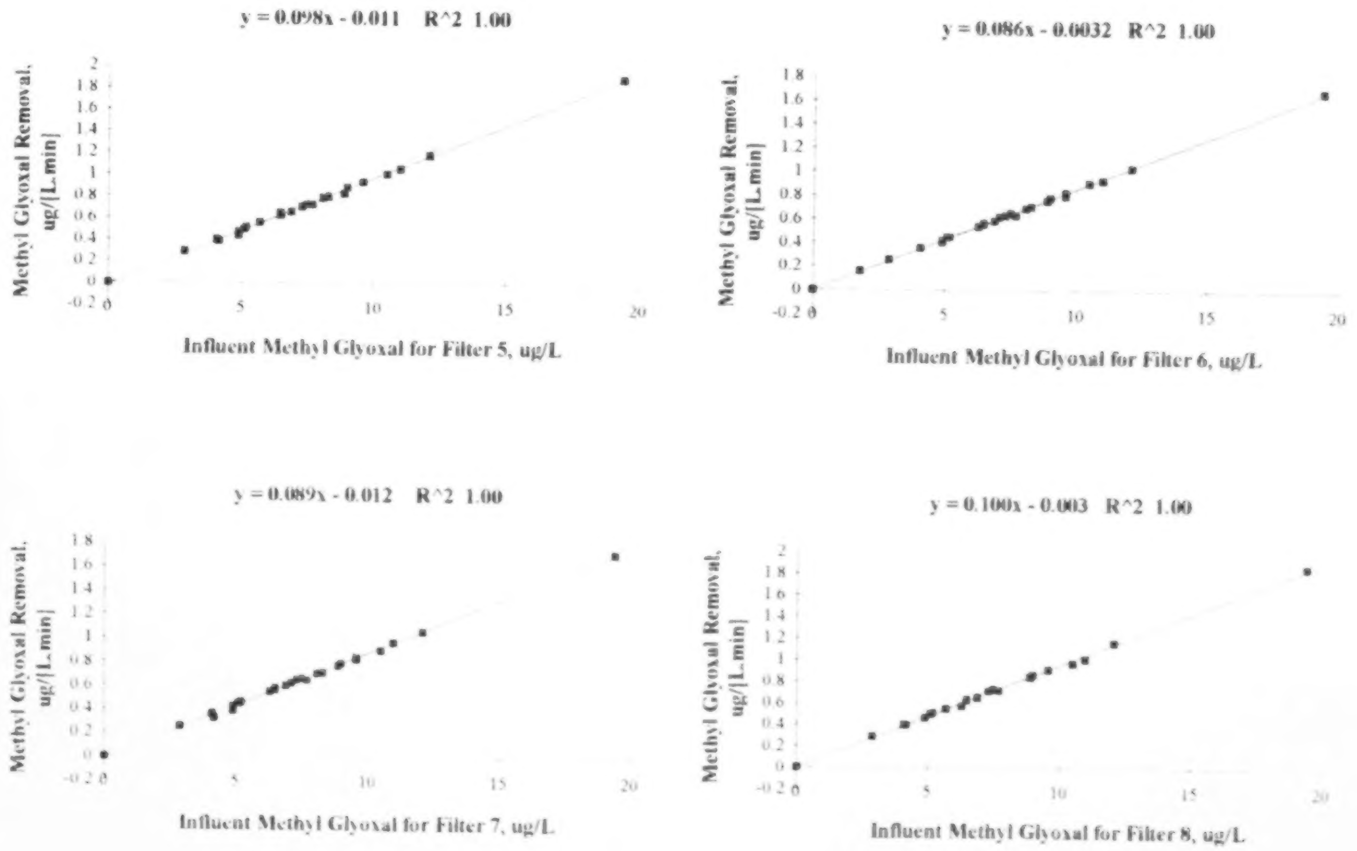


Figure B51   Methyl Glyoxal Removal Rate vs Influent Concentration for Filters 5-8, Edmonton, Alberta 1992-1993 Study

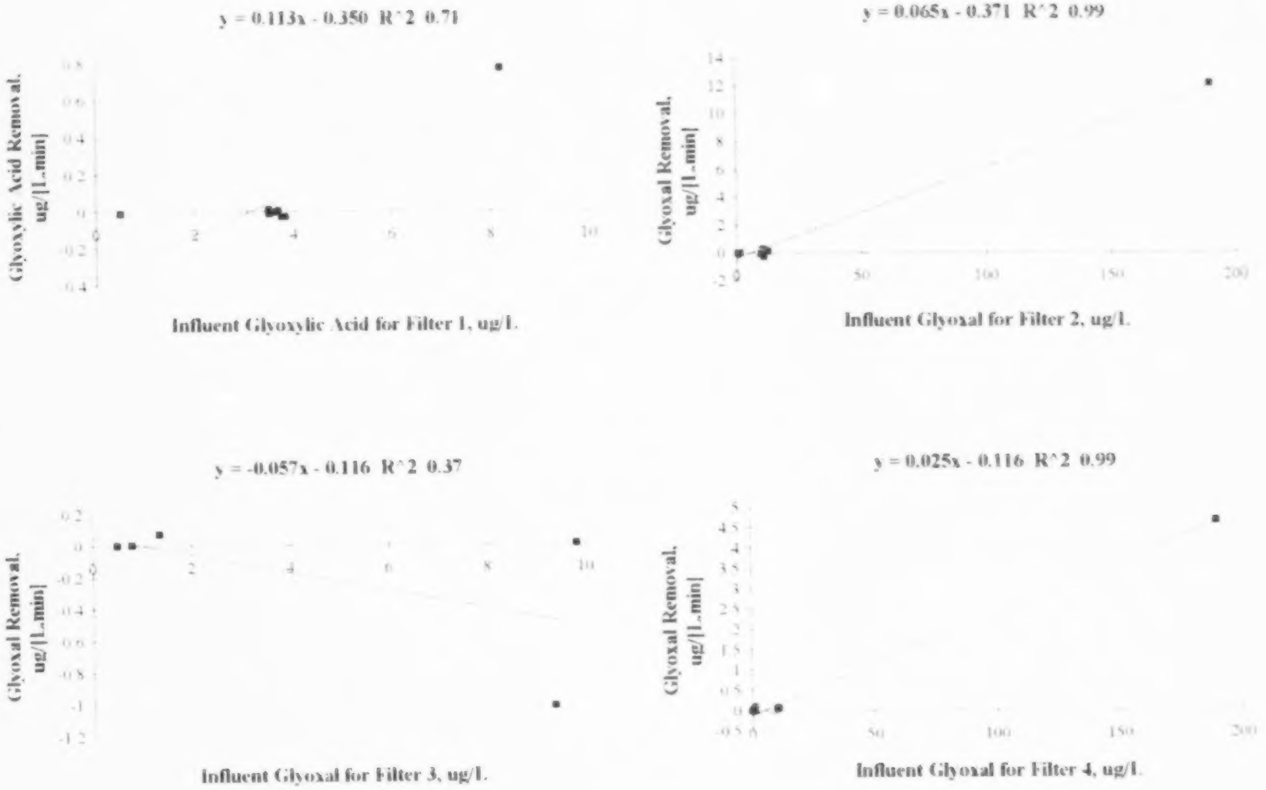
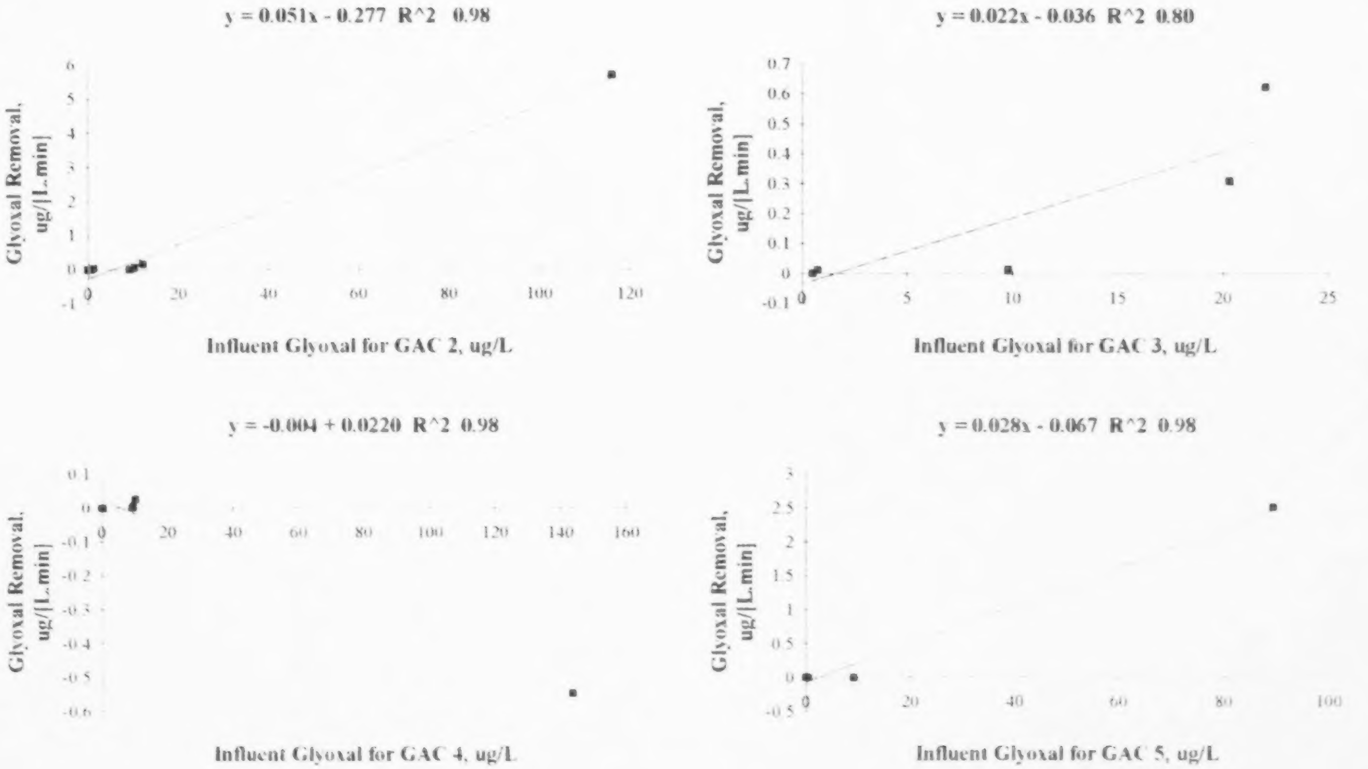


Figure B52 Glyoxal Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study


y = 0.051x - 0.277 R^2 0.98

y = 0.022x - 0.036 R^2 0.80

y = -0.004 + 0.0220 R^2 0.98

y = 0.028x - 0.067 R^2 0.98

Figure B53 Glyoxal Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

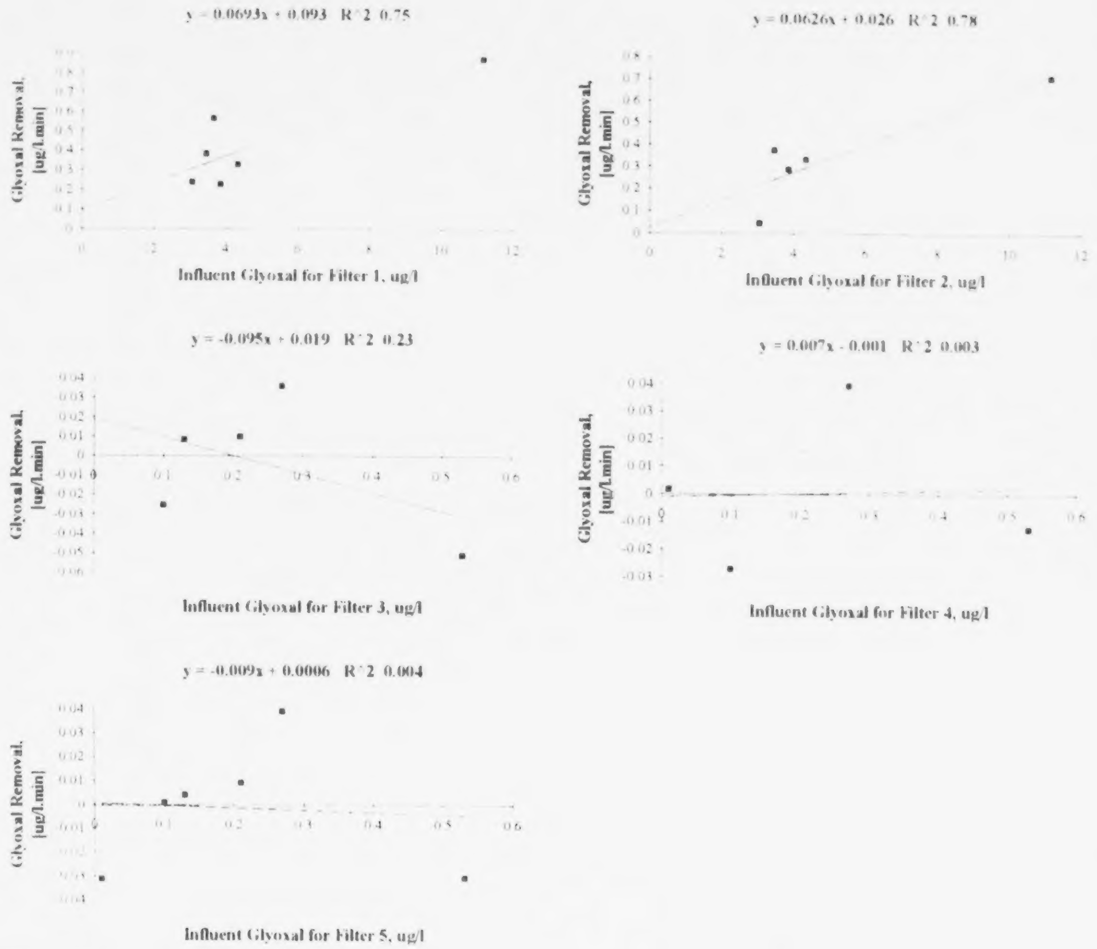


Figure B54 Glyoxal Removal Rate vs Influent Concentration for Filters, Woodbridge, CT Study

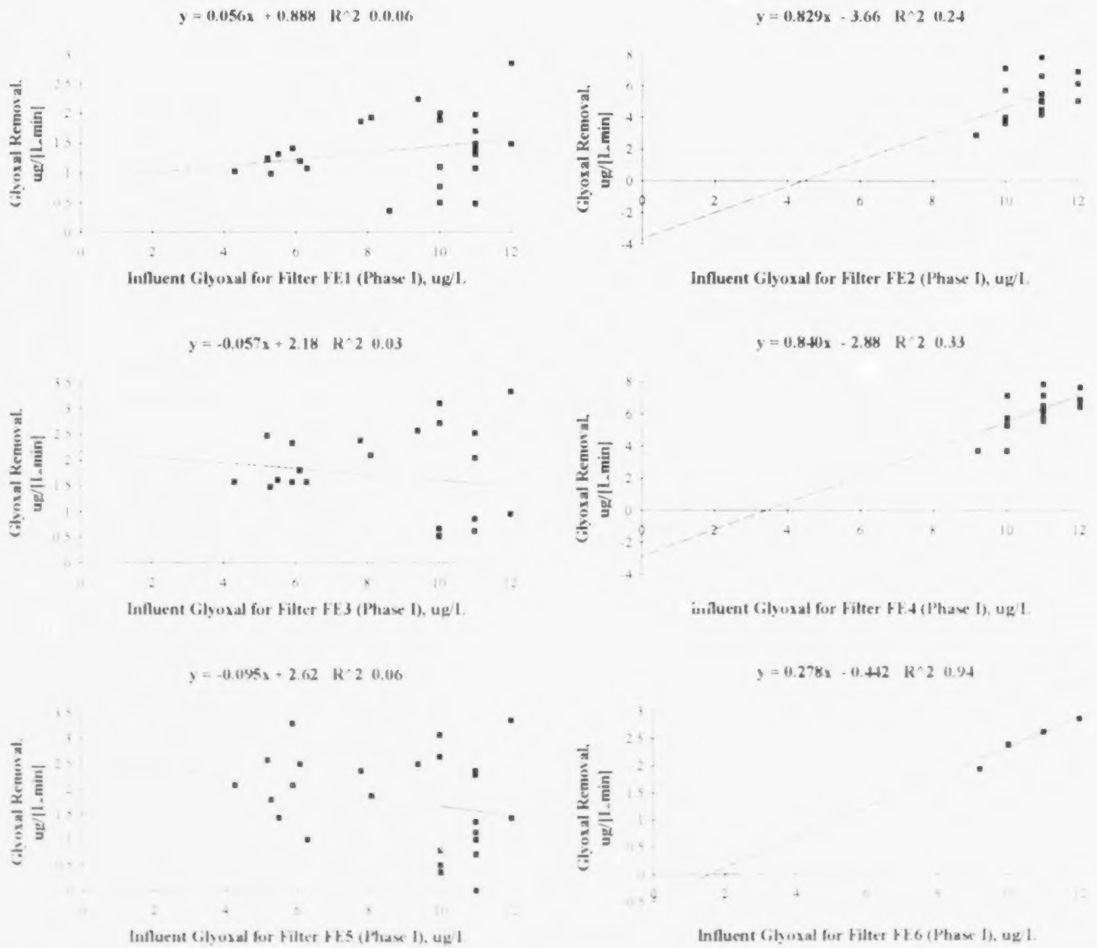


Figure B55 Glyoxal Removal Rate vs Influent Concentration for Filters (Phase I), Southern California Study

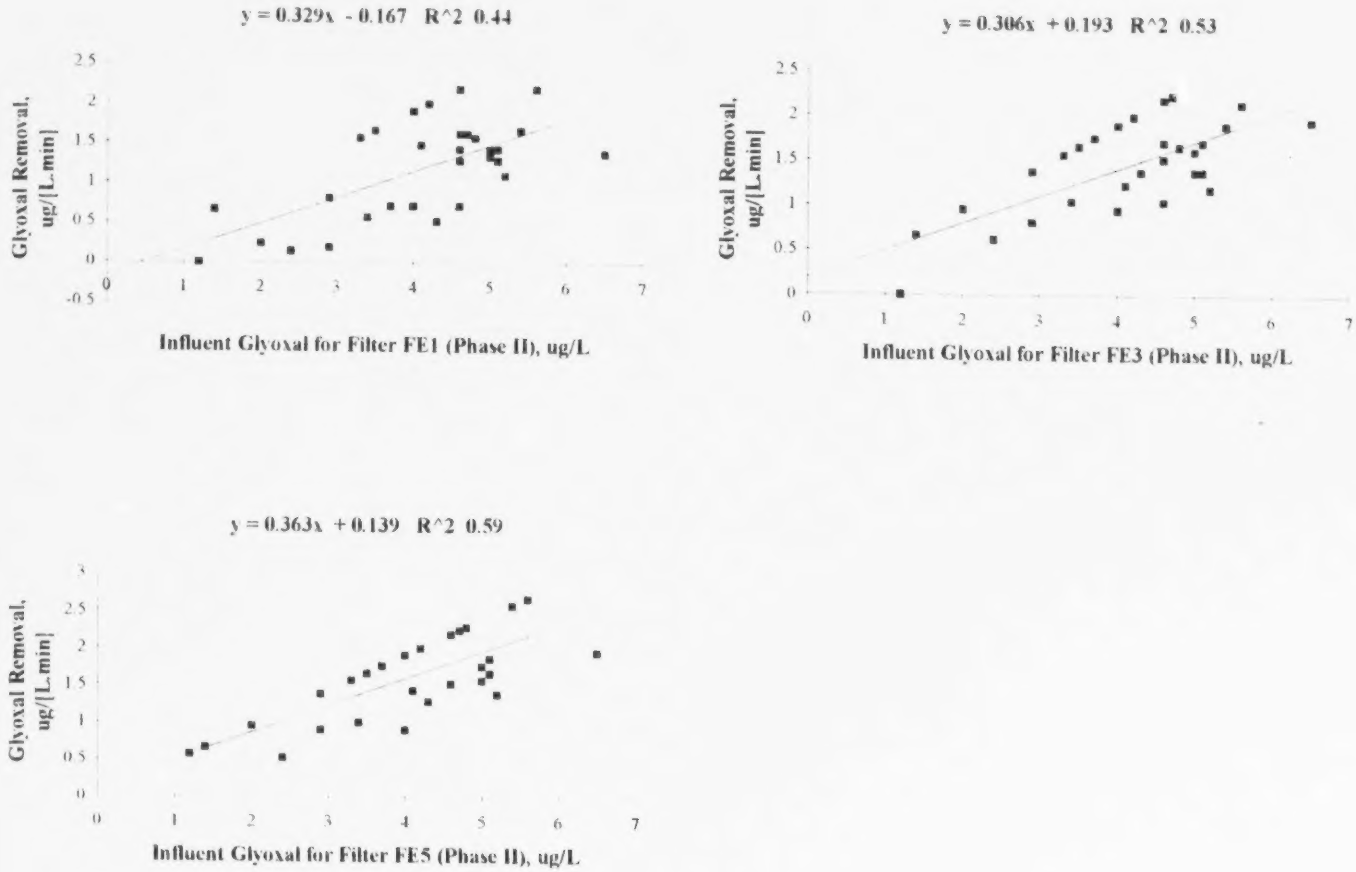


Figure B56. Glyoxal Removal Rate vs. Influent Concentration for Filters (Phase II), Southern California Study

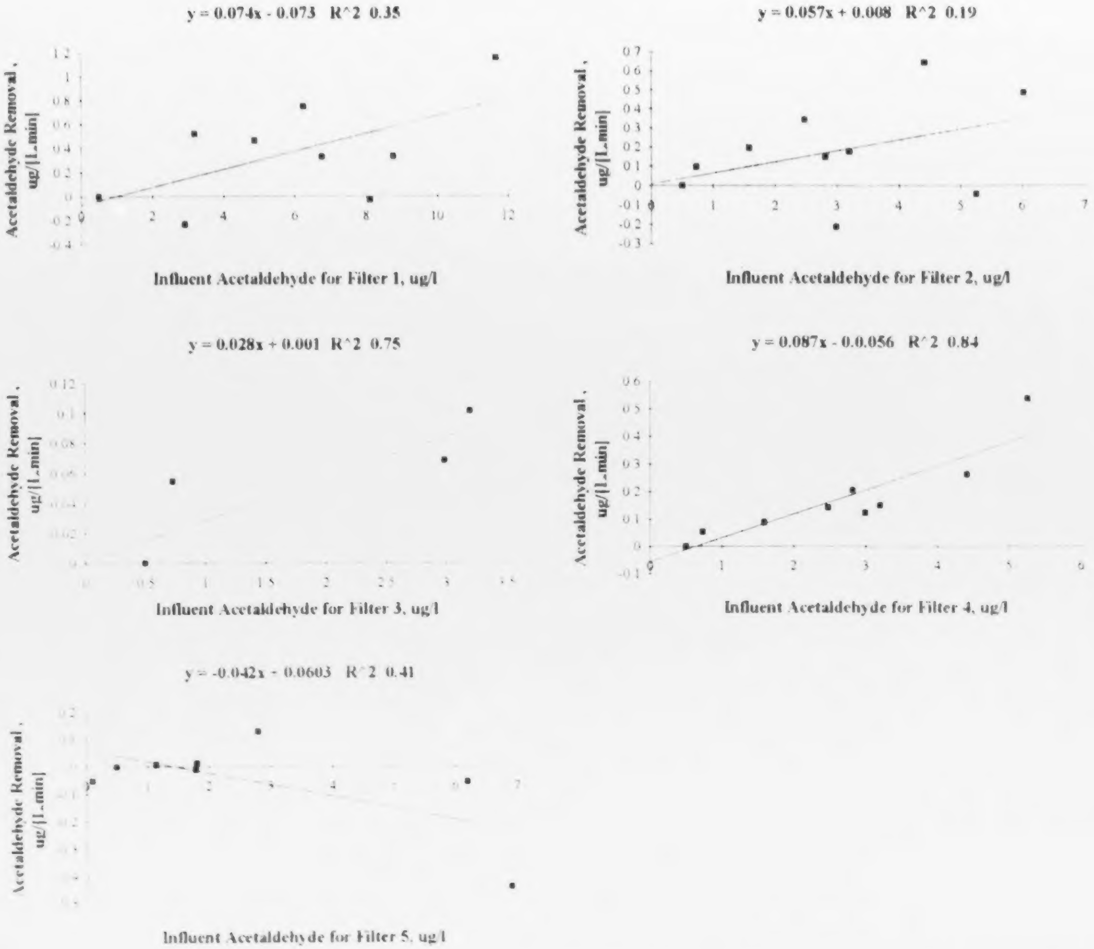


Figure 57 Acetaldehyde Removal Rate vs Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

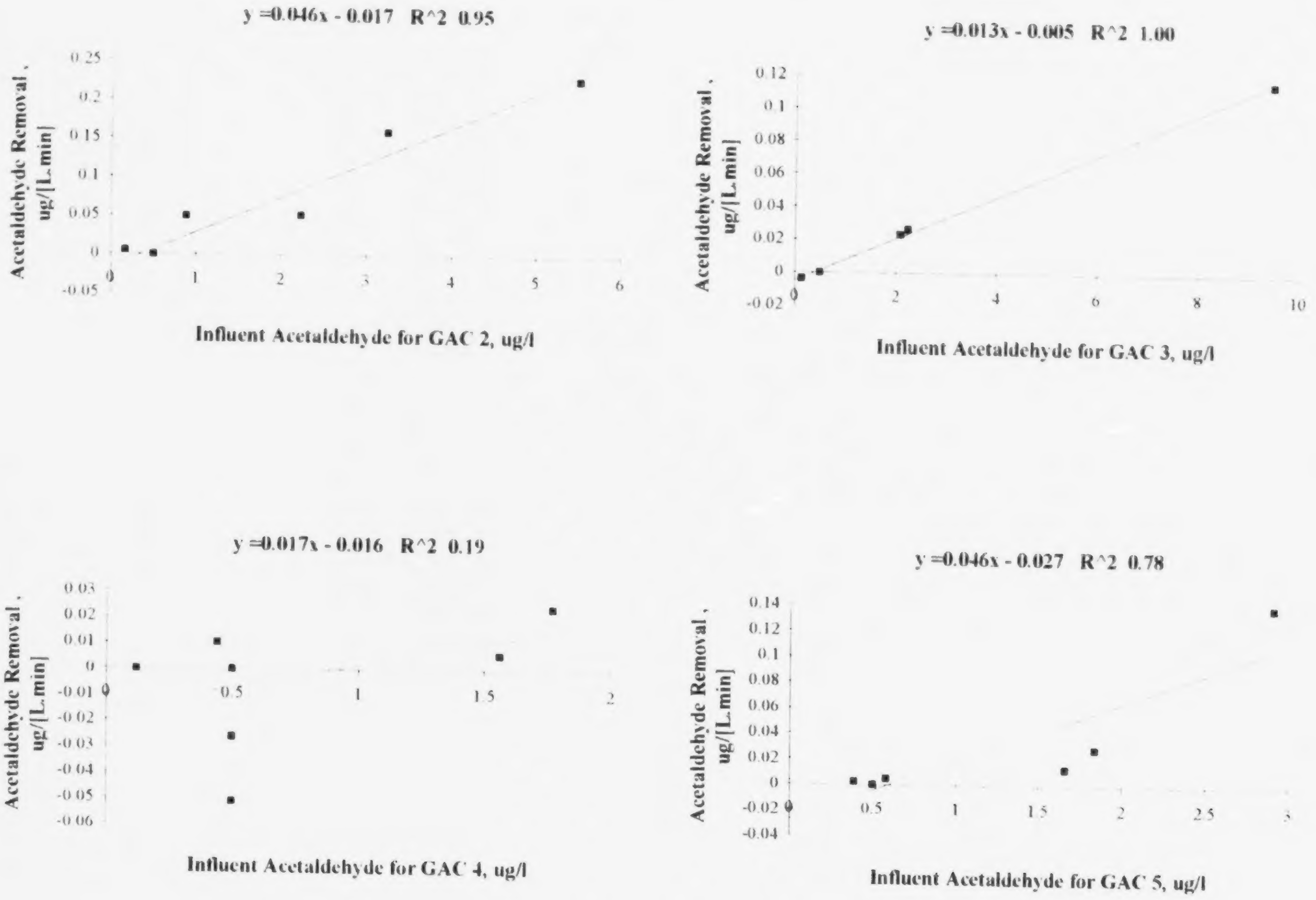


Figure B58: Acetaldehyde Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

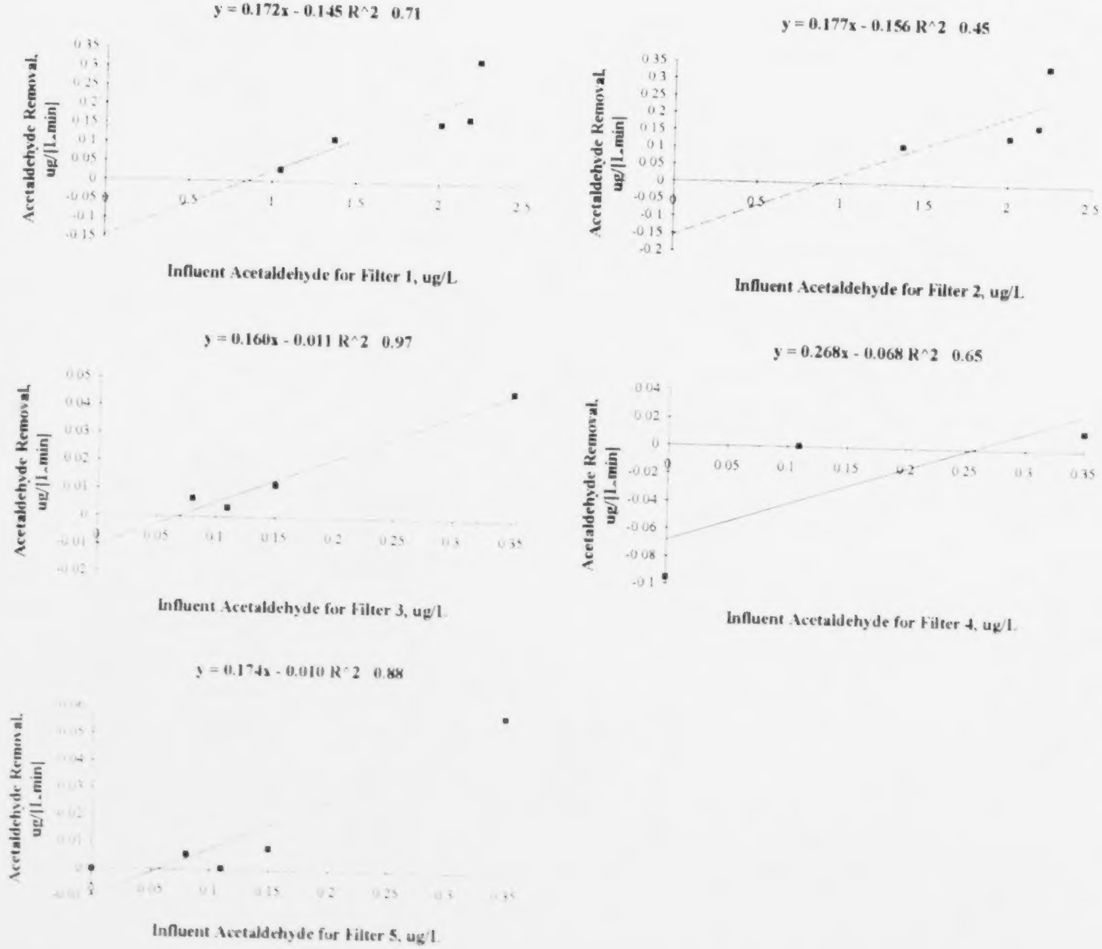


Figure 59 Acetaldehyde Removal Rate vs. Influent Concentration for Filters, Woodbridge, CT Study

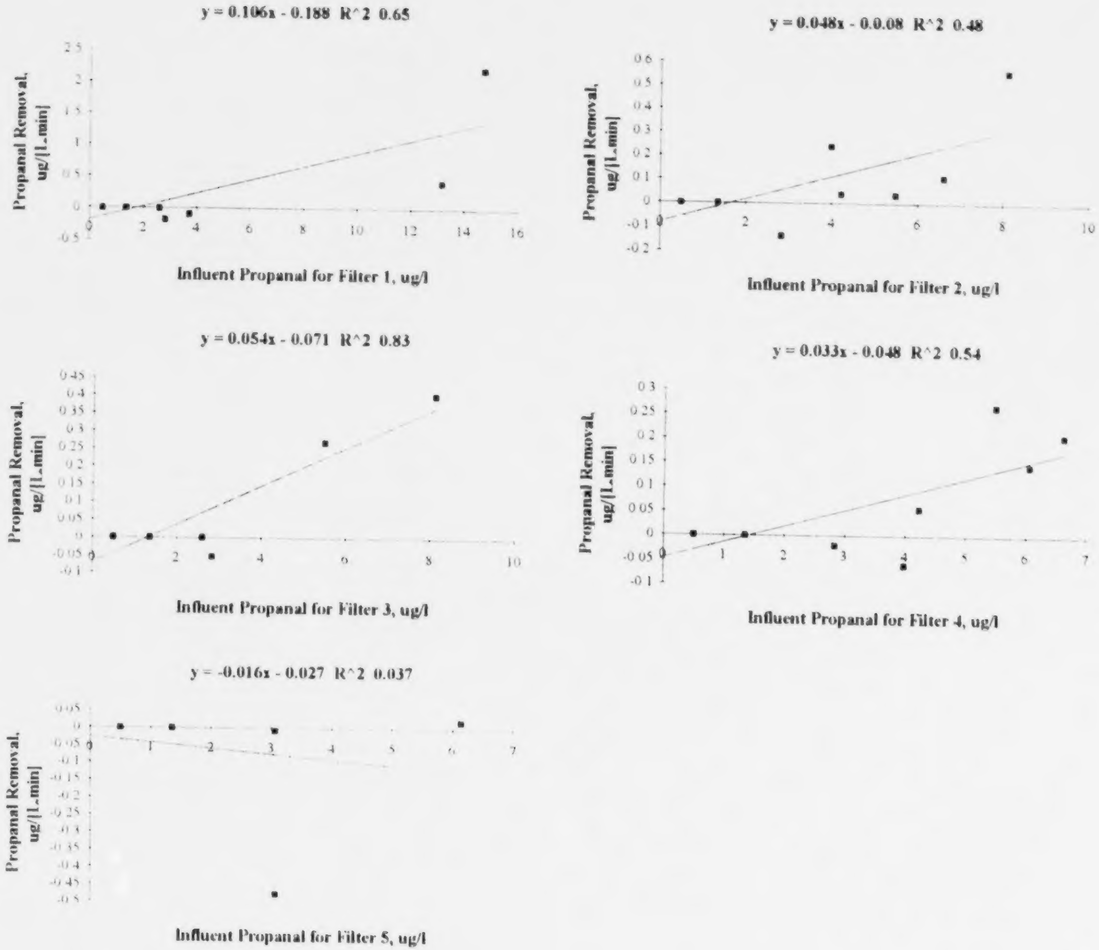


Figure B60: Propanal Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

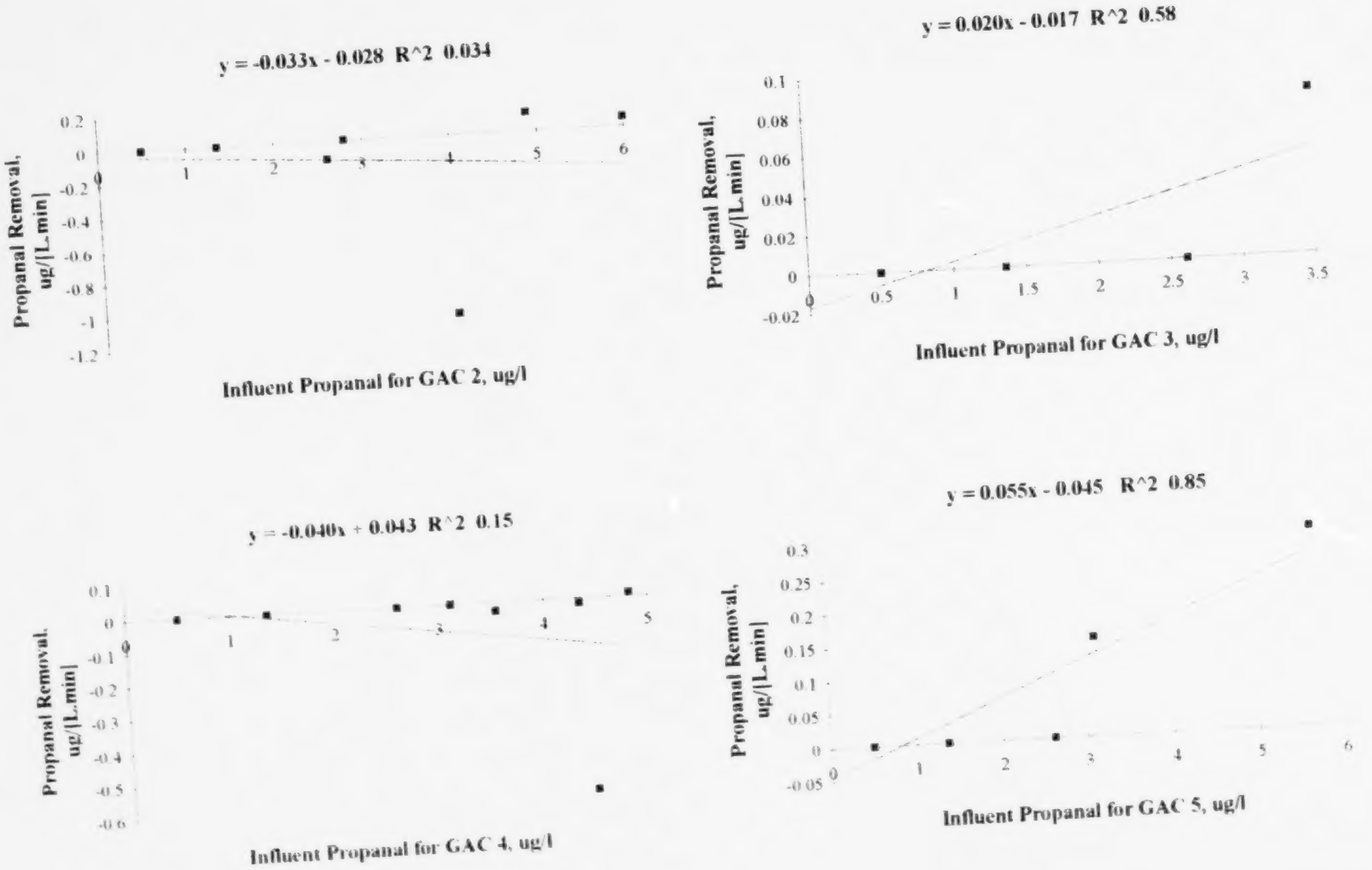


Figure B61: Propanal Removal Rate vs. Influent Concentration for GAC Contactors for Edmonton, Alberta, 1992-1993 Study

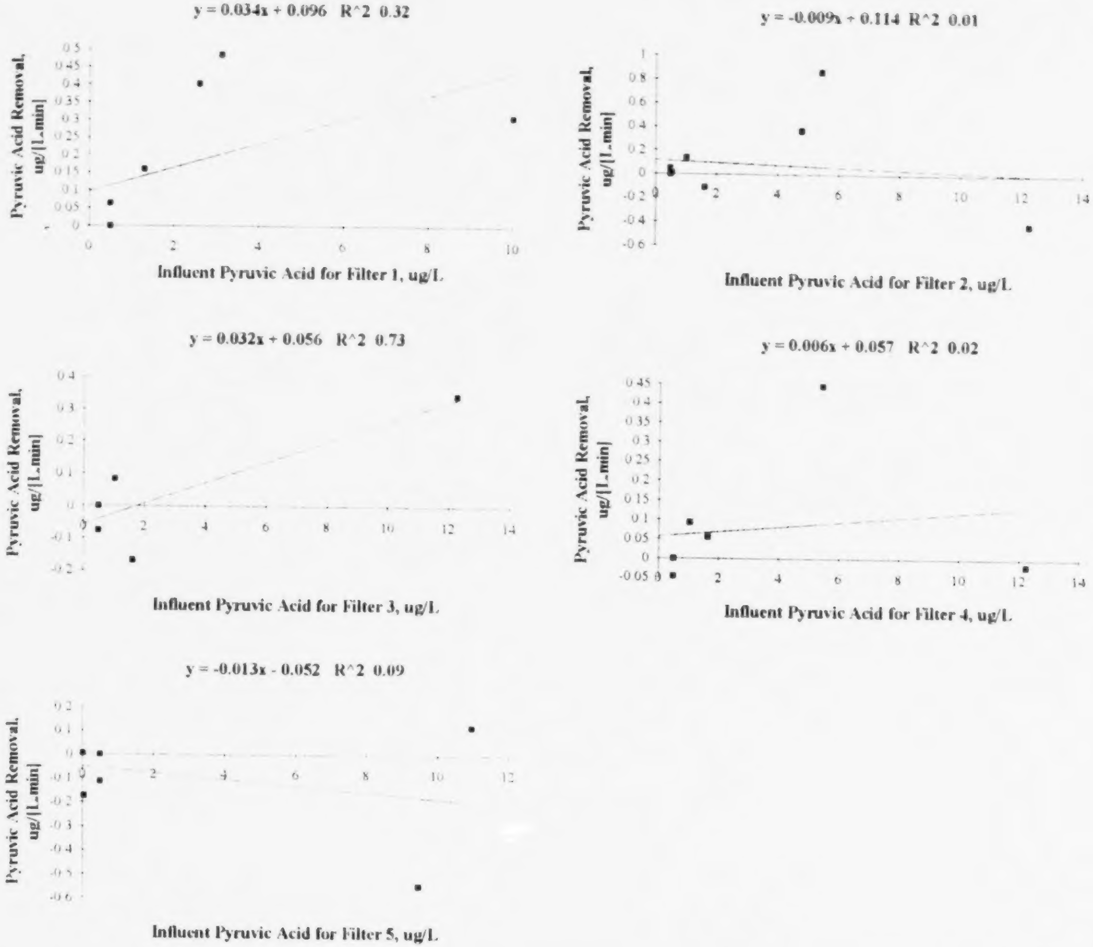


Figure B63: Pyruvic Acid Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

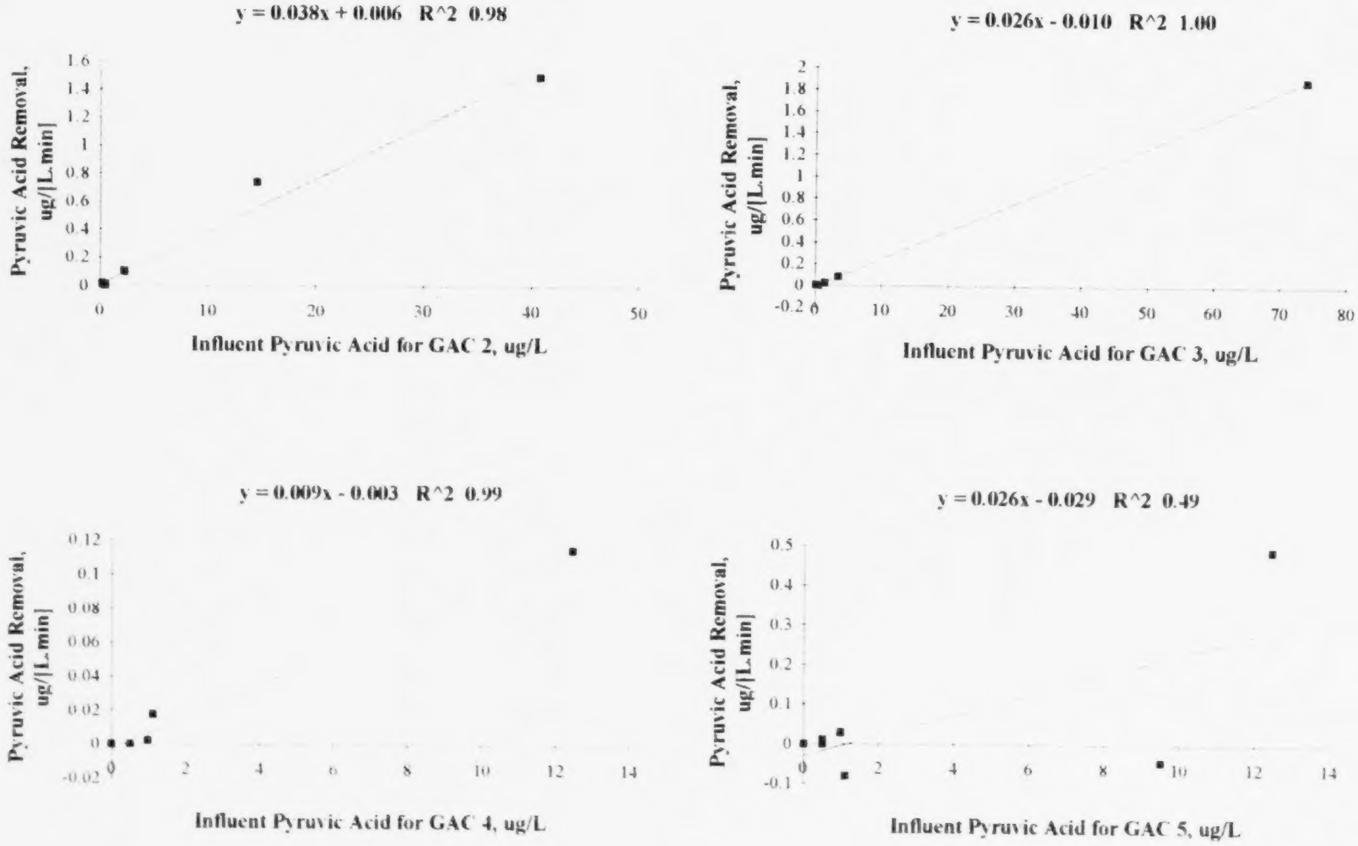


Figure B63 Pyruvic Acid Removal Rate vs Influent Concentration fir GAC Contactors, Edmonton, Alberta 1992-1993 Study

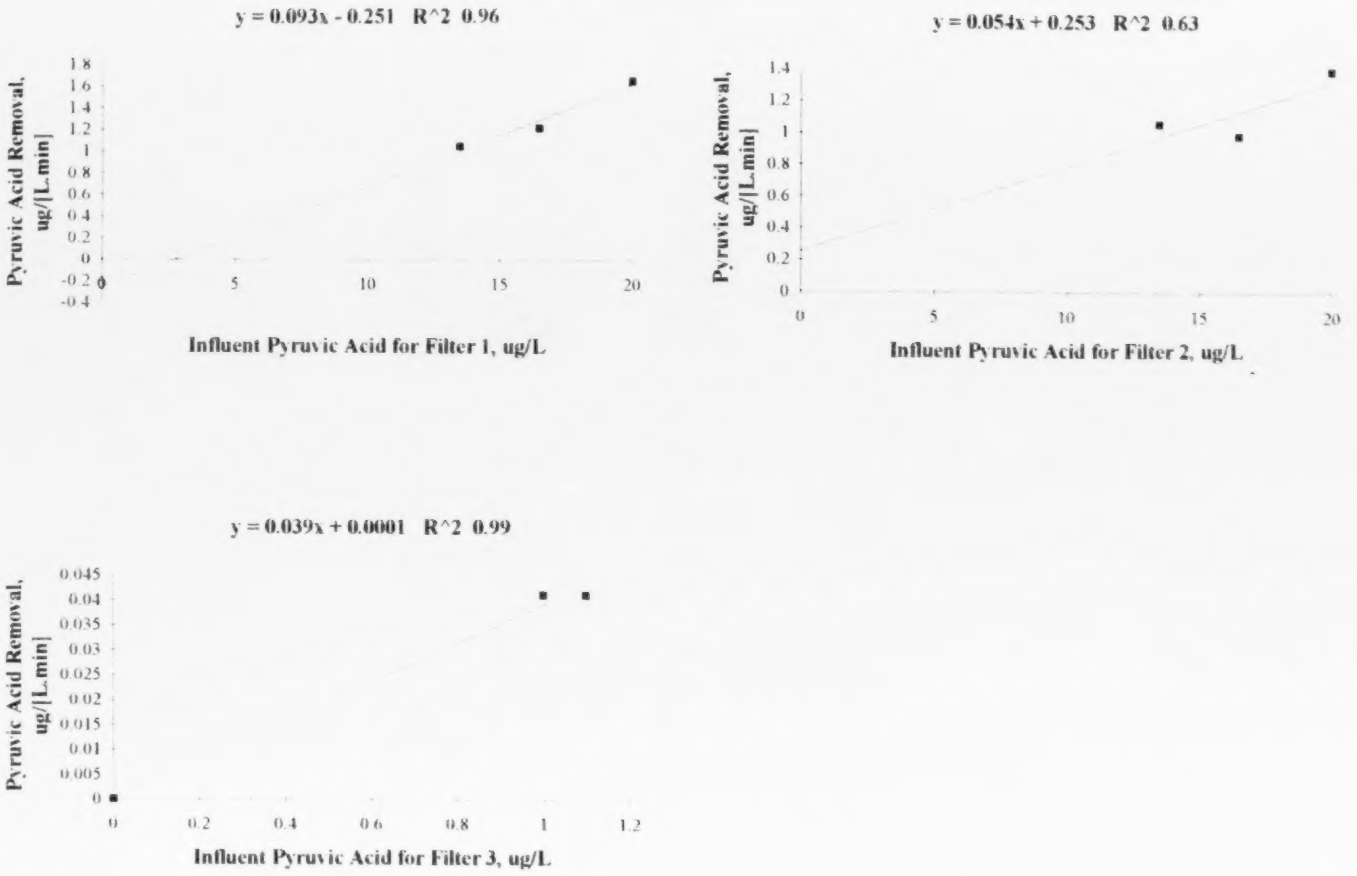


Figure B64: Pyruvic Acid Removal Rate vs. Influent Concentration for Filters, Woodbridge CT Study

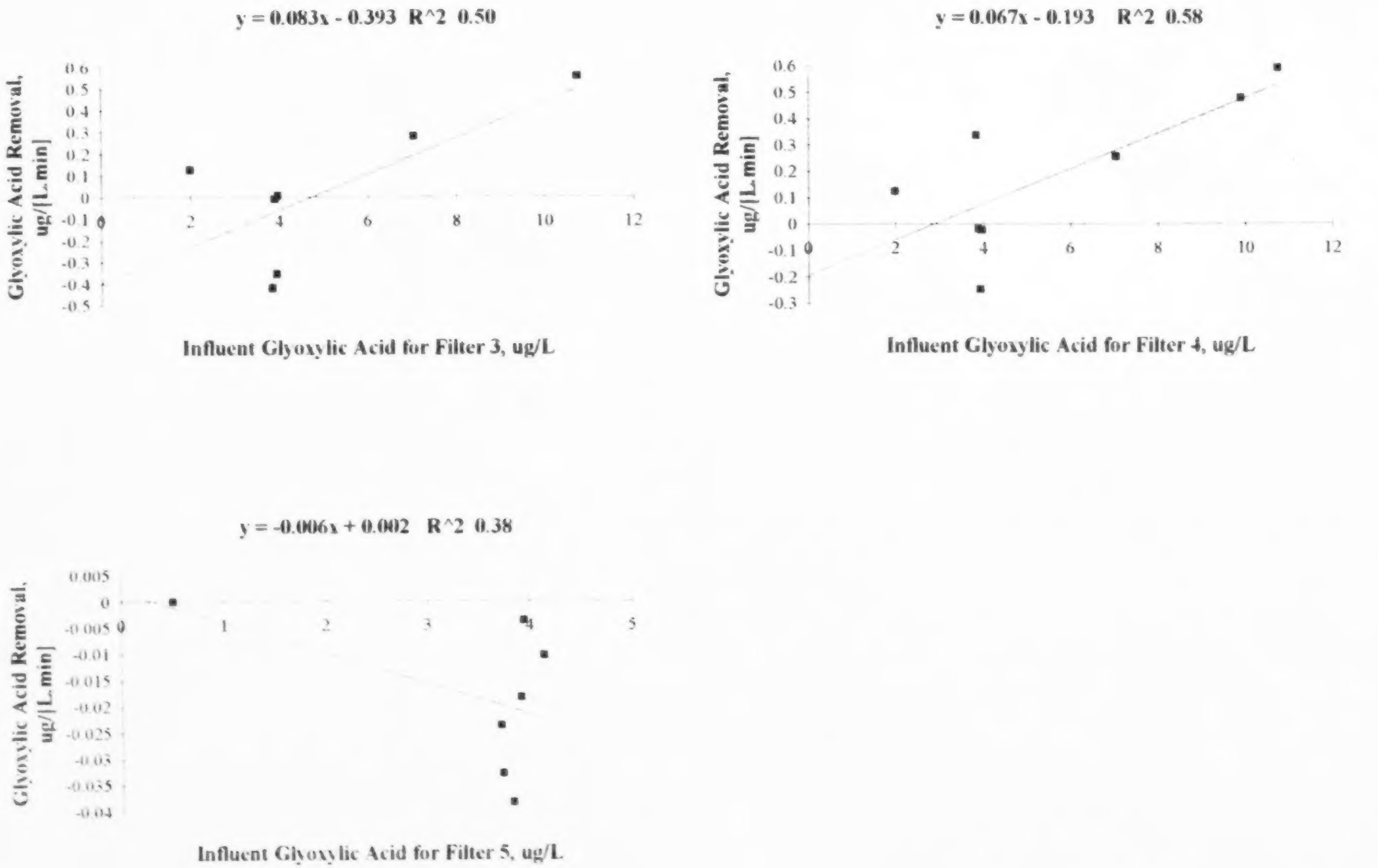


Figure B65 Glyoxylic Acid Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

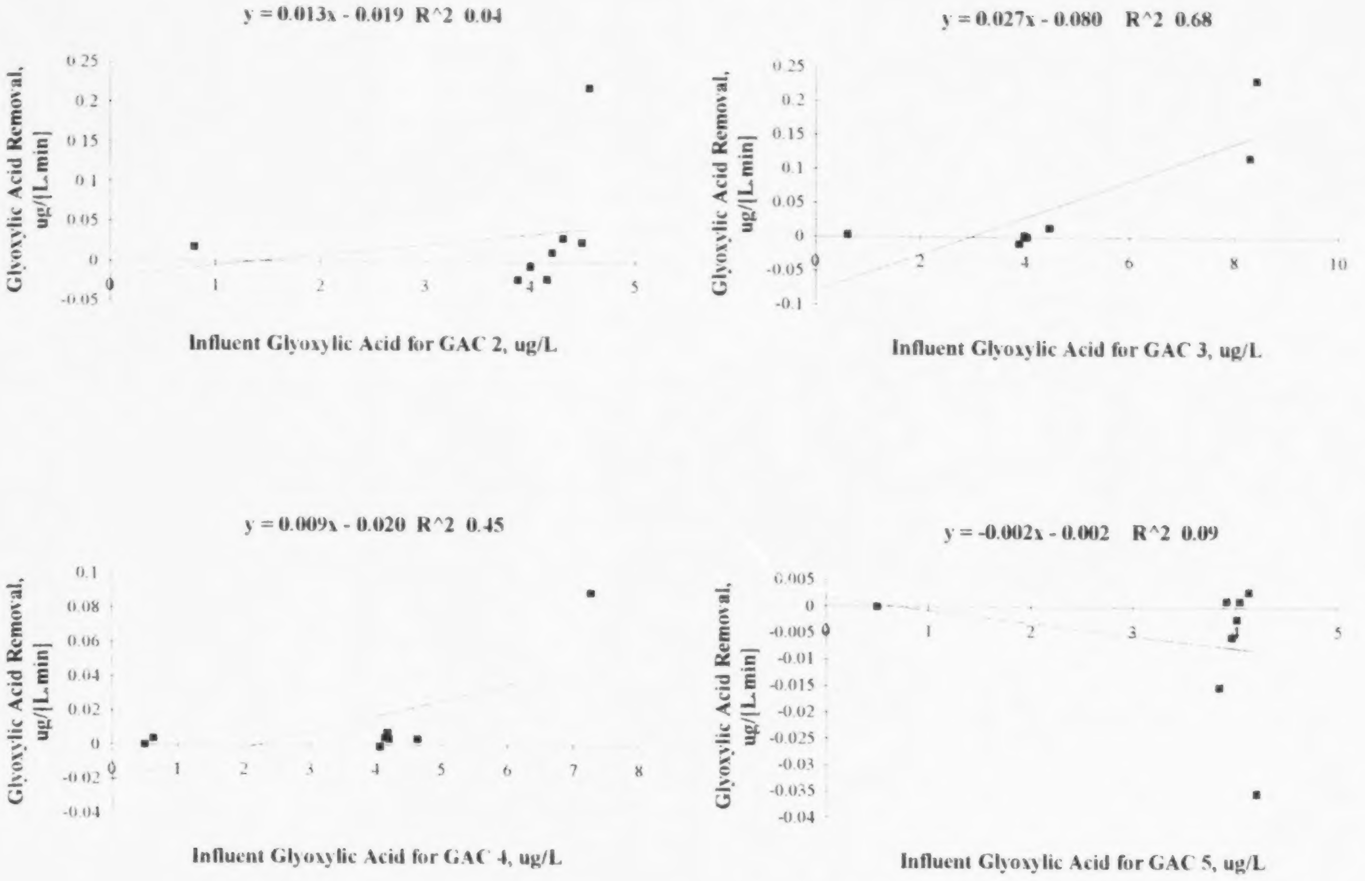


Figure B66: Glyoxylic Acid Removal Rate vs. Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993

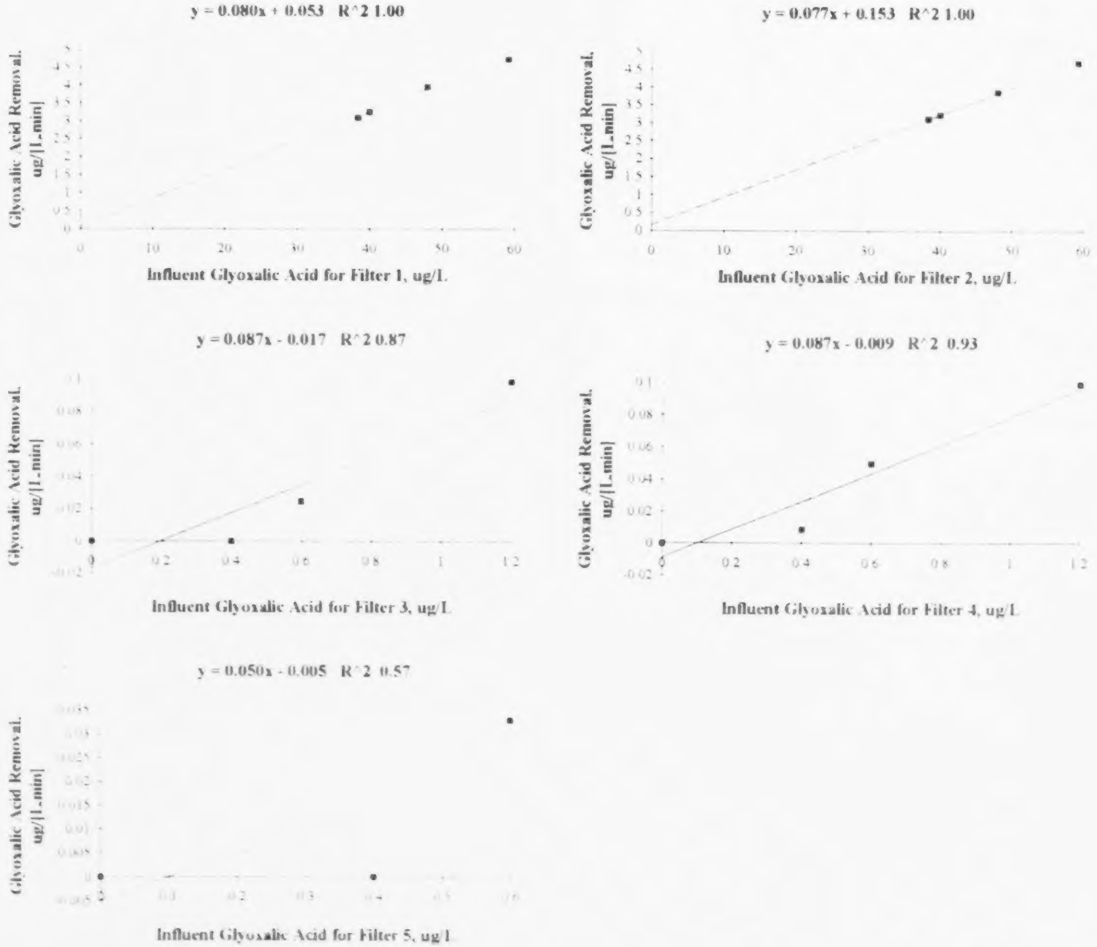


Figure B67 Glyoxylic Acid Removal Rate vs. Influent Concentration for Filters, Woodbridge, CT Study

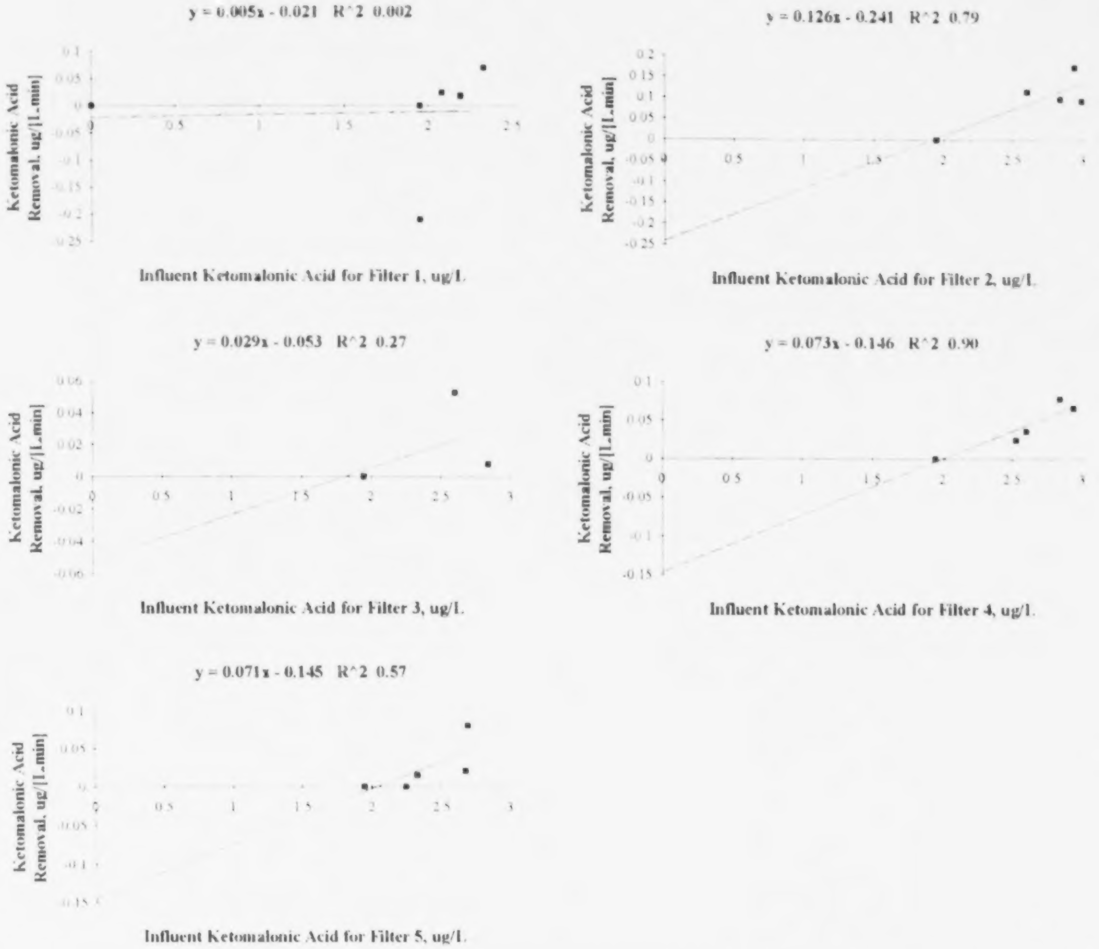


Figure B68 Ketomalonic Acid Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993

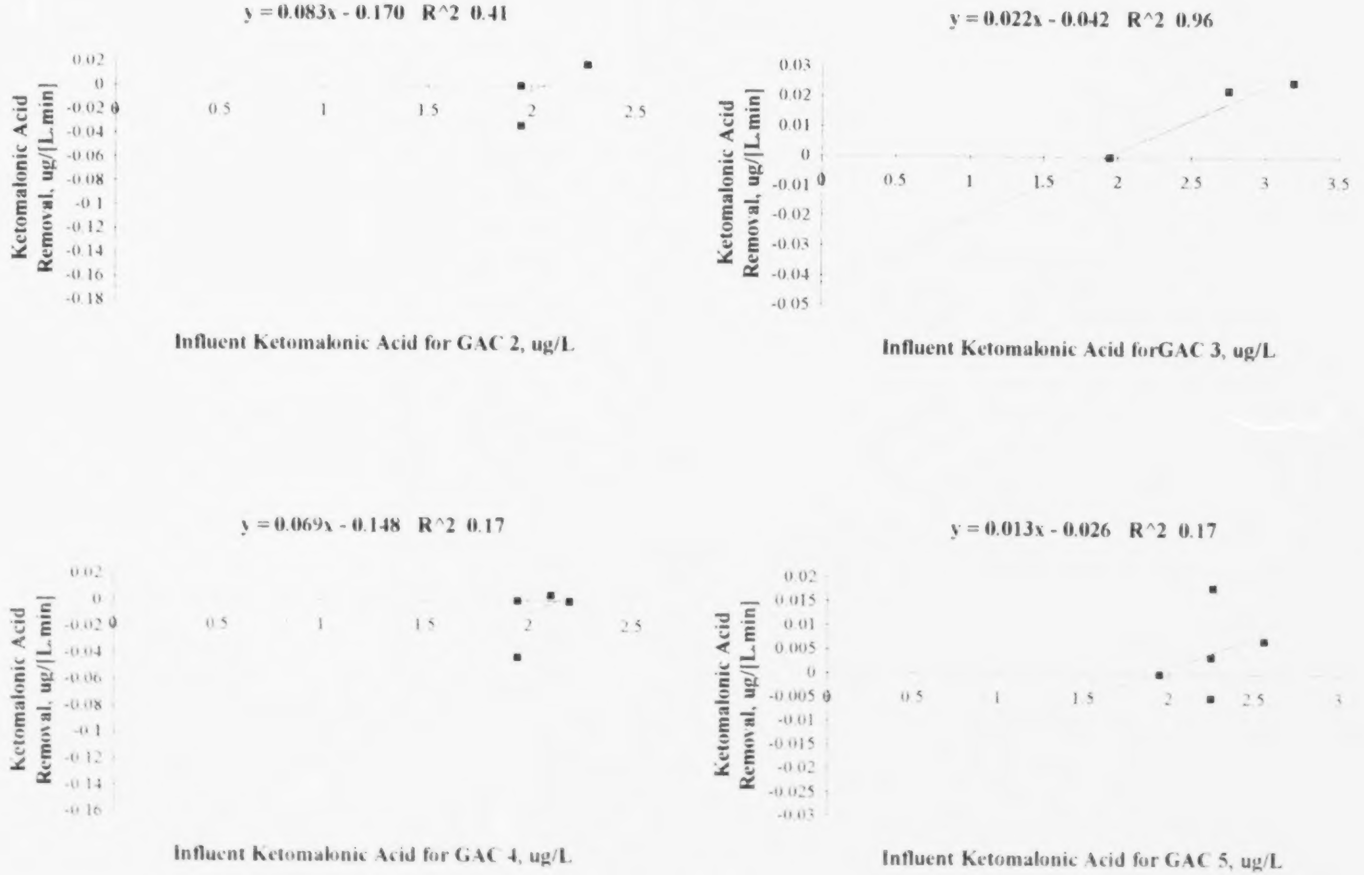


Figure B69 Ketomalonic Acid Removal Rate vs Influent Concentration for GAC Contactors , Edmonton, Alberta 1992-1993 Study

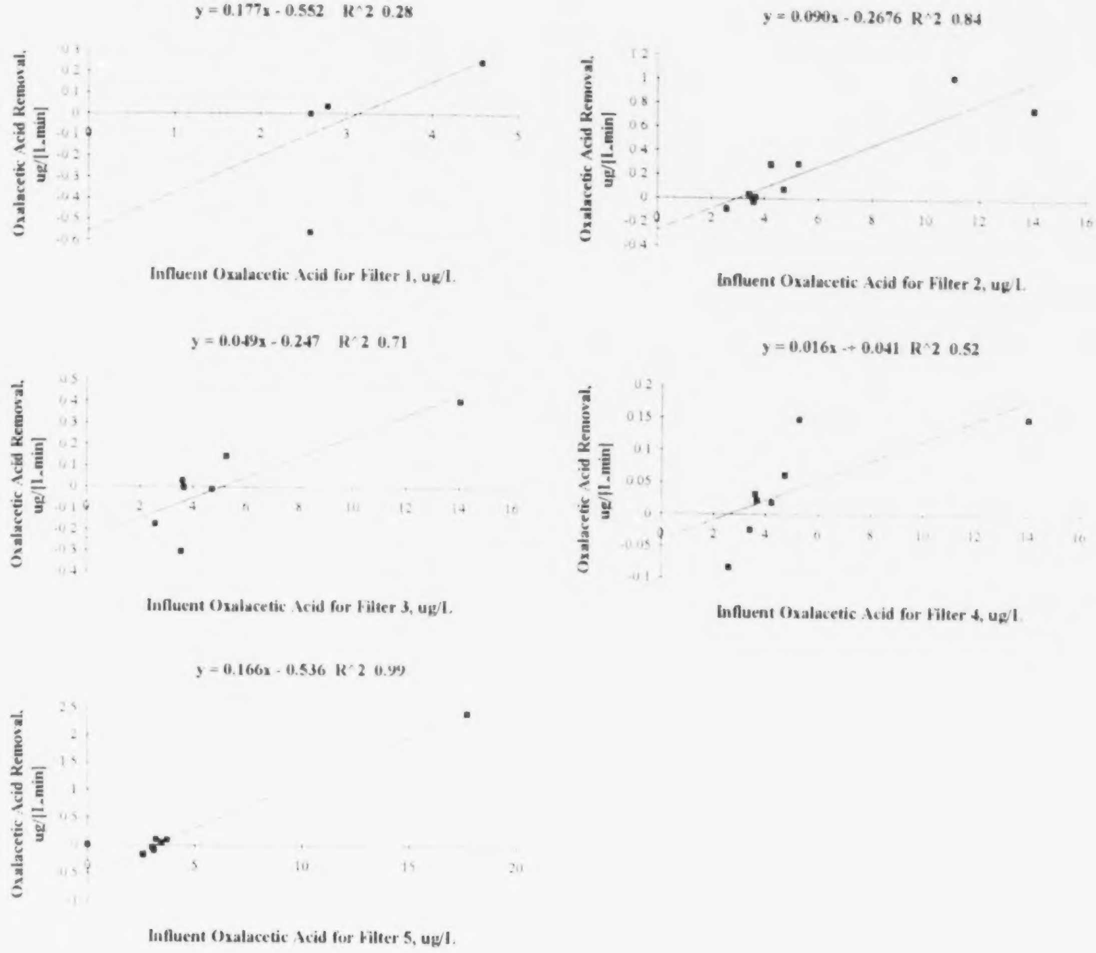


Figure B70 Oxalacetic Acid Removal Rate vs. Influent Concentration for Filters, Edmonton, Alberta 1992-1993 Study

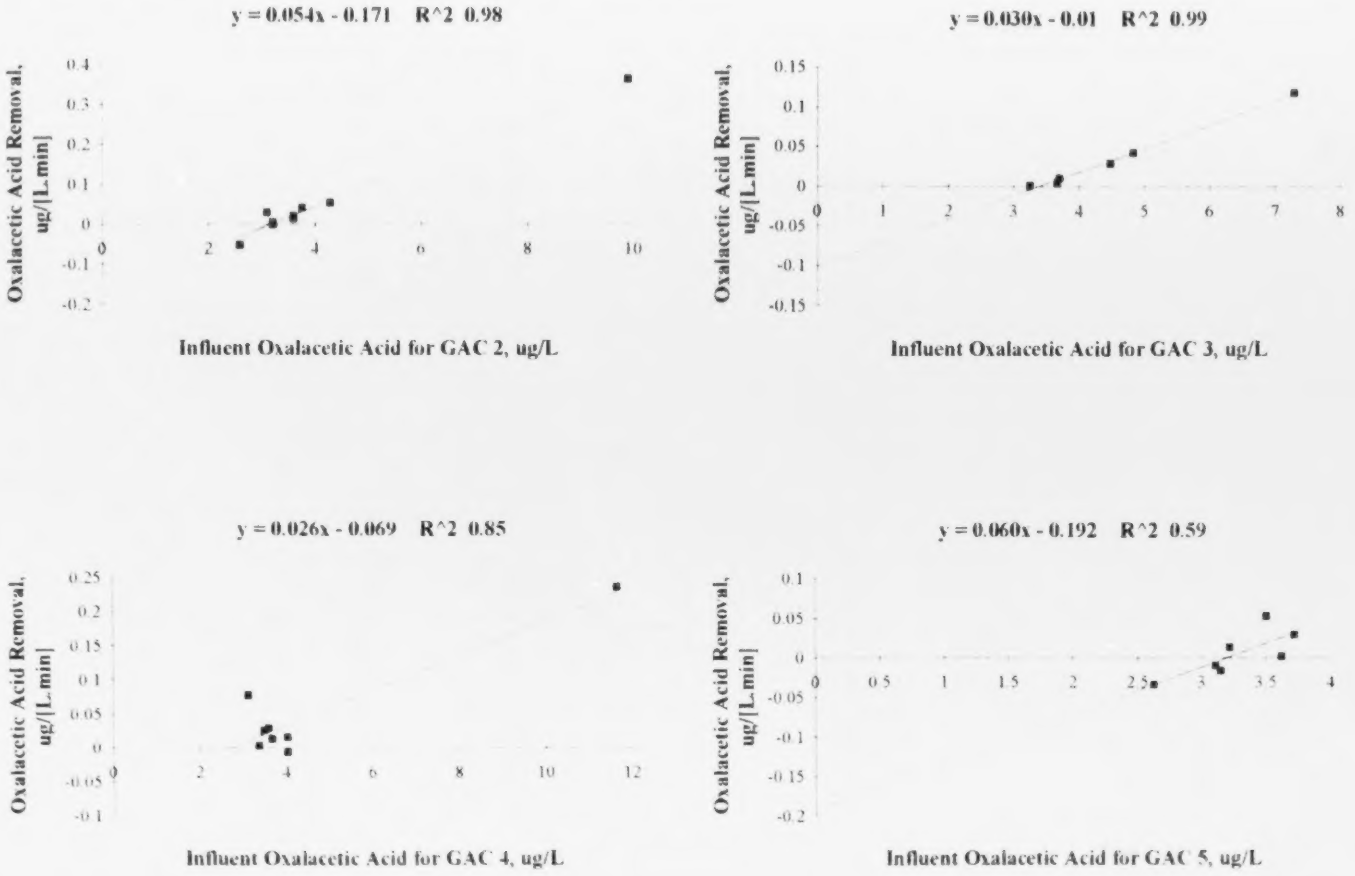


Figure B71 Oxalacetic Acid Removal Rate vs Influent Concentration for GAC Contactors, Edmonton, Alberta 1992-1993 Study

APPENDIX C

C.1 Oxoacids

Oxoacids were determined for both the Edmonton 1992-1993 study and the Woodbridge, CT study. Both studies cited the same reference when describing their experimental protocol. Therefore their methods are assumed to be similar.

Because of the generally poor correlations observed, due in part to small numbers of data points, this discussion and analysis is contained in Appendix C. In summary it was found that all oxo-acids analyses produced results showing poor linearity. It appeared that the apparent rate constants were independent of EBCT. The oxo-acids are not recommended to be modeled using this empirical approach.

C.1.1 Pyruvic Acid

Edmonton, Alberta Study, 1992-1993

The parameter pyruvic acid was analyzed in the Edmonton study. These apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 49. Unfortunately, fewer data points were available for this parameter and often the plots consisted of the majority of the points around the x-intercept and few point showing higher removal rates. The plots for all filters and GAC contactors are found in Appendix B, Figures B62 and B63.

Table C-1
Pyruvic Acid Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.034± 0.050	-2.8	0.096 ± 0.192	0.57‡	5.29-5.46
Filter 2	-0.009± 0.71	12.7	0.114± 0.325	0.10‡	5.46-6.07
Filter 3	0.032± 0.027	1.8	-0.056 ± 0.138	0.85†	10.77-11.3
Filter 4	0.006± 0.044	-9.3	0.056 ± 0.225	0.16‡	8.83-15.7
Filter 5	-0.013± 0.016	-4.0	-0.052 ± 0.218	0.29‡	5.89-5.47
GAC 2	0.038± 0.004	0.2	0.006± 0.058	0.99	17.19-18.40
GAC 3	0.026± 1.7e-4	0.4	-0.010± 0.005	1.00	34.5-38.76
GAC 4	0.010± 0.006	0.3	-0.003± 0.007	0.99	34.50-42.72
GAC 5	0.026 ± 0.023	1.1	-0.029 ± 0.122	0.70†	17.25-17.31

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, all the filters showed poor correlation and all correlation coefficients were not significant at the 5% level except for Filter 3. The apparent rate constants for these filters were low and negative in some cases. The second stage filtration indicated better correlation, with all correlation coefficients being significant at the 5% level or better. The graphical relationship for GAC 2 is displayed in Figure 88.

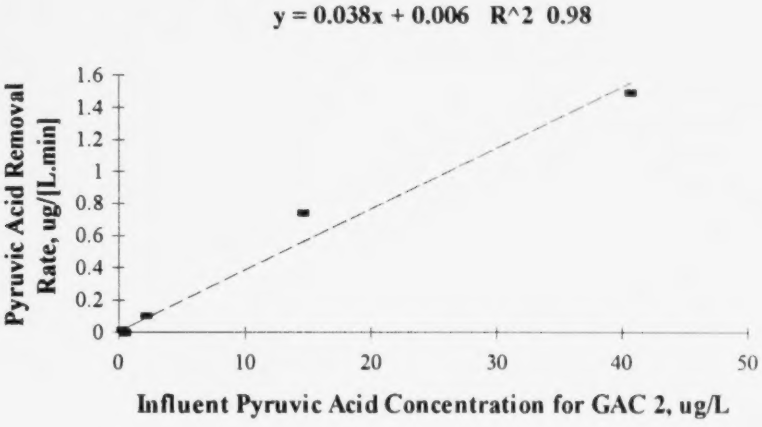


Figure C1: Pyruvic Acid Removal Rate vs. Influent Concentration for GAC 2, Edmonton, Alberta, 1992-1993

Woodbridge, CT Study

This study determined pyruvic for the influent and effluent locations for only three filters. Unfortunately, only three data points were available for each filter. The calculated apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 50. All filters except Filter 3 produced results not significant at the 5% level. Filter 3 produced a good linear relationship and had a correlation coefficient of 0.99. The graphical relationship for Filter 1 is shown in Figure 89. The plots for all filters are found in Appendix B, Figure B64

Table C-2
Pyruvic Acid Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.093 ± 0.235	0.8	-0.251± 3.968	0.98‡	6.2-12.2
Filter 2	0.054 ± 0.517	0.1	0.264± 8.731	0.79‡	6.2-12.2
Filter 3	0.039 ± 0.041	0.1	1.9e-4 ± 0.035	0.99†	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.
† The correlation coefficient is significant at the 5% level but not the 1% level
‡ The correlation coefficient is not significant at the 5% level

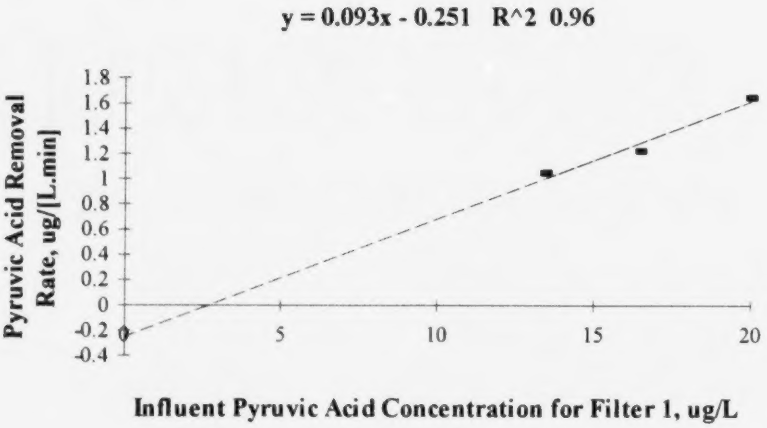


Figure C2: Pyruvic Acid Removal Rate vs. Influent Concentration for Filter 1, Woodbridge, CT Study

C.1.2 Glyoxylic Acid

Edmonton, Alberta Study, 1992-1993

The parameter glyoxylic acid was analyzed in the Edmonton study. The apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 51. The plots for all filters and GAC contactors are found in Appendix B, Figures B65 and B66.

Table C-3

Glyoxylic Acid Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.113± 0.064	3.1	-0.350 ± 0.270	0.85	5.29-5.46
Filter 2	0.080 ± 0.033	1.7	-0.139± 0.263	0.85	5.46-6.07
Filter 3	0.083± 0.095	4.8	-0.394 ± 0.242	0.71‡	10.77-11.3
Filter 4	0.067± 0.055	2.9	-0.193 ± 0.364	0.76†	8.83-15.7
Filter 5	-0.006± 0.008	0.3	0.002 ± 0.025	0.61‡	5.89-5.47
GAC 2	0.013± 0.009	1.5	-0.019± 0.208	0.21‡	17.19-18.40
GAC 3	0.027 ± 0.021	3.0	-0.080± 0.116	0.83†	34.5-38.76
GAC 4	0.009± 1.6e-4	2.2	-0.020± 0.043	0.67‡	34.50-42.72
GAC 5	-0.002± 0.007	1.0	0.002 ± 0.021	0.29‡	17.25-17.31

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, only Filter 1(chlorinated stream) and Filter 2 (ozonated stream) produced correlation coefficients significant at the 1% level. The apparent rate constants were 0.113 and 0.080 min^{-1} for Filters 1 and 2 respectively. For the remaining filters and GAC contactors the data indicated a high degree of scatter and resulted in correlation coefficients not significant at the 5% level except GAC 3. The graphical relationship for Filter 2 is shown in Figure 90.

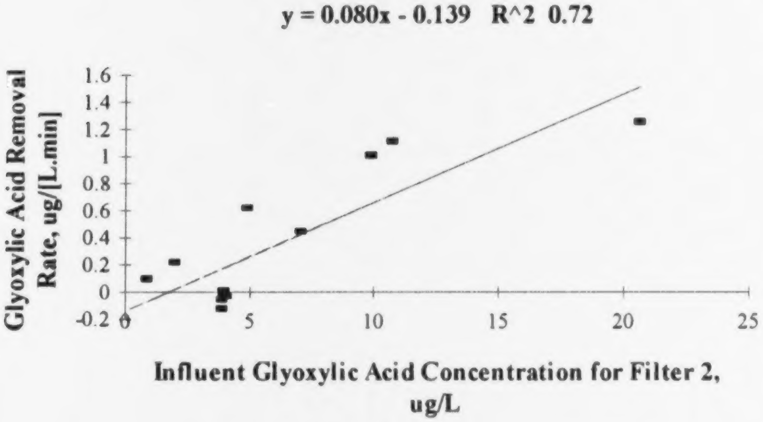


Figure C3: Glyoxylic Acid Removal Rate vs. Influent Concentration for Filter 2, Edmonton, Alberta 1992-1993

Woodbridge, CT Study

This study determined glyoxylic acid for the influent and effluent locations for five filters. The calculated apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 52. All filters except Filter 1 and 2 produced results not significant at the 1% level. These filters were ozonated and Filter 2 was backwashed with chlorinated water. The linear relationship for Filter 2 is shown in Figure 91. The plots for all filters are found in Appendix B, Figure B67.

Table C-4

Glyoxylic Acid Summary for Woodbridge, CT Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.080 ± 0.015	-0.7	0.053± 0.699	1.00	6.2-12.2
Filter 2	0.077 ± 0.004	-2.0	0.153± 0.175	1.00	6.2-12.2
Filter 3	0.087 ± 0.102	0.2	-0.017 ± 0.071	0.93‡	6.2-12.2
Filter 4	0.087± 0.068	0.1	-0.009 ± 0.052	0.96†	6.2-12.2
Filter 5	0.050 ± 0.517	0.1	-0.005 ± 0.215	0.74‡	6.2-12.2

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

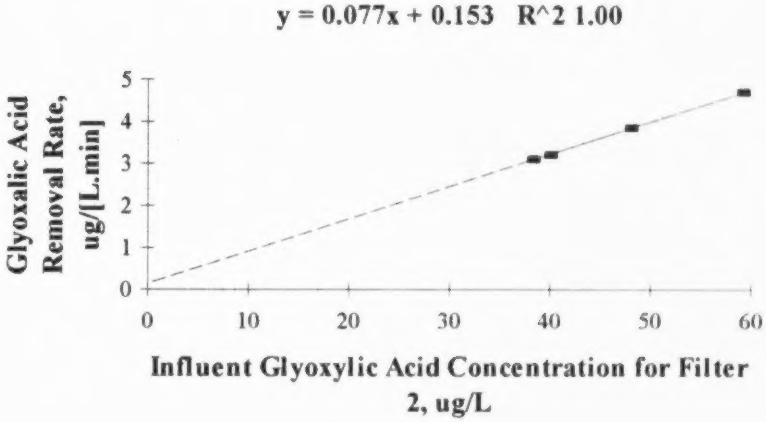


Figure C4: Glyoxylic Acid Removal Rate vs. Influent Concentration for Filter 2, Woodbridge CT Study

C.1.3 Ketomalonic Acid

Edmonton, Alberta Study, 1992-1993

The parameter ketamalonic acid was analyzed in the Edmonton study. These apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 53. Unfortunately, fewer data points were available for this parameter and often the plots consist of the majority of points around the x-intercept and a few points showing higher removal rates. The plots for all filters and GAC contactors are found in Appendix B, Figures B68 and B69.

Table C-5

Ketomalonic Acid Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (μg/L)	y-Intercept* (μg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.005± 0.112	4.2	-0.021 ± 0.216	0.05‡	5.29-5.46
Filter 2	0.126 ± 0.091	1.9	-0.241± 0.234	0.89†	5.46-6.07
Filter 3	0.029± 0.145	1.8	-0.052 ± 0.343	0.52‡	10.77-11.3
Filter 4	0.073± 0.035	2.0	-0.146 ± 0.087	0.95	8.83-15.7
Filter 5	0.071± 0.085	2.	-0.145 ± 0.199	0.88†	5.89-5.47
GAC 2	0.083± 0.184	2.0	-0.170± 0.032	0.64‡	17.19-18.40
GAC 3	0.022 ± 0.008	1.9	-0.042± 0.091	0.98‡	34.5-38.76
GAC 4	0.069± 0.280	2.1	-0.148± 0.570	0.41‡	34.50-42.72
GAC 5	-0.013± 0.034	2.0	-0.026 ± 0.073	0.41‡	17.25-17.31

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration, Filters 1 (chlorinated stream), and Filter 3 (ozonated stream) produced correlation coefficients not significant at the 5% level. The correlation coefficients for Filter 2 (ozonated) and Filter 5 (non-ozonated) were only significant at the 5% level and Filter 4 (filter adsorber) was significant at the 1% level. The apparent rate constants varied between 0.071 to 0.126 min^{-1} for streams showing significant correlation. All x-intercepts were approximately in the same range. The second stage filtration indicated linear correlations not significant at the 5% level. The graphical relationship for Filter 4 is shown in Figure 92. Although the second stage filtration indicated poor linearity, it would appear that some removal of ketomalonic acid is being achieved.

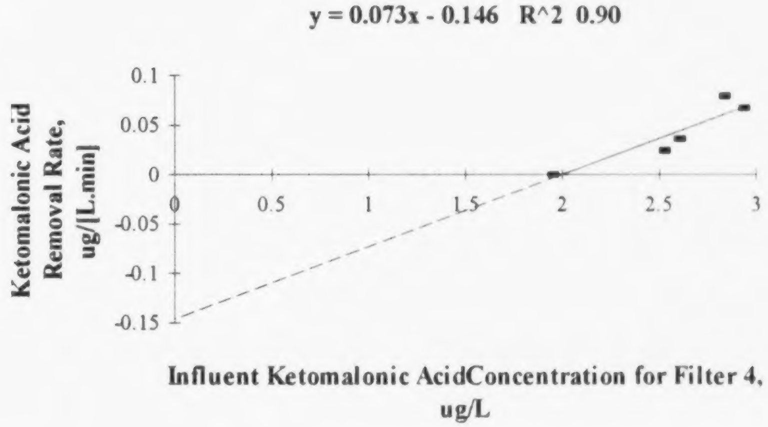


Figure C5: Ketamalonic Acid Removal Rate vs. Influent Concentration for Filter 4, Edmonton, Alberta 1992-1993

C.1.4 Oxalacetic Acid

Edmonton, Alberta Study, 1992-1993

The parameter oxalacetic acid was analyzed in the Edmonton study. These apparent rate constants, x-intercepts, y-intercepts and correlation coefficients are given in Table 54. The plots for all filters and GAC contactors are found in Appendix B, Figure B70 and B71.

Table C-6

Oxalacetic Acid Summary for Edmonton, 1992-93 Study

Stream	Apparent Rate* Constant (min^{-1})	x-Intercept (µg/L)	y-Intercept* (µg/L.min)	Correlation Coefficient r	EBCT (min)
Filter 1	0.177± 0.323	3.0	-0.552 ± 0.965	0.53‡	5.29-5.46
Filter 2	0.089 ± 0.032	3.0	-0.267± 0.215	0.91	5.46-6.07
Filter 3	0.049± 0.036	5.0	-0.247 ± 0.232	0.84†	10.77-11.3
Filter 4	0.016± 0.015	2.6	-0.041 ± 0.094	0.72†	8.83-15.7
Filter 5	0.166± 0.013	3.2	-0.536 ± 0.092	0.99	5.89-5.47
GAC 2	0.054± 0.006	3.2	-0.171± 0.028	0.99	17.19-18.40
GAC 3	0.030 ± 0.003	3.4	-0.101± 0.018	0.99	34.5-38.76
GAC 4	0.026± 0.011	2.7	-0.069± 0.058	0.92	34.50-42.72
GAC 5	0.060± 0.057	3.2	-0.192 ± 0.190	0.77†	17.25-17.31

* Apparent first order rate constants and y-intercept are shown with 95% confidence intervals

Correlation coefficients are significant at the 1% level, unless otherwise noted.

† The correlation coefficient is significant at the 5% level but not the 1% level

‡ The correlation coefficient is not significant at the 5% level

For the first stage filtration only Filter 1 (chlorinated stream) resulted in a correlation coefficient not significant at the 5% level. The remaining filters had correlation coefficients significant at the 5% level or better. The apparent rate constants ranged between 0.016 and 0.166 min^{-1} for filters with significant linearity. The graphical presentation for Filter 2 is shown in Figure 93. The second stage filters all indicated good linearity, however when observing the actual plots in Appendix B, it was discovered that most of the data points were at the x-intercept and only one data point indicated a higher removal rate. This leads to some question of the validity of the analysis of these data.

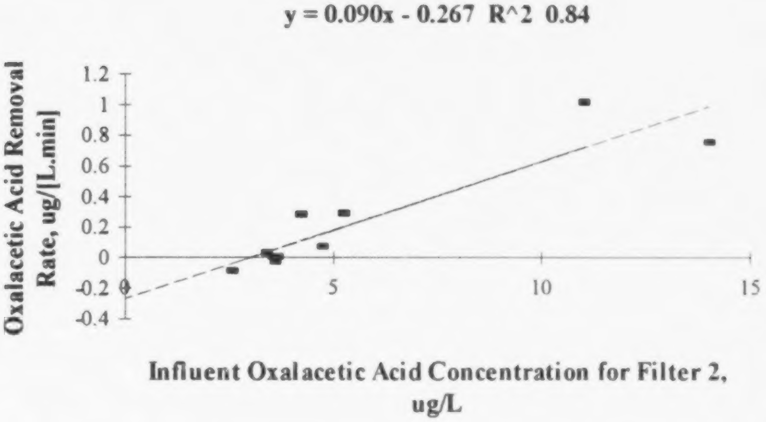


Figure C6: Oxalacetic Acid Removal Rate vs. Influent Concentration Filter 2, Edmonton, Alberta 1992-1993

All the oxo-acid analyses produced results showing poor linearity. It appeared that the apparent rate constants were independent of EBCT, since the Woodbridge study produced some significant linear results, when two hydraulic loading rates were employed. The oxo-acids are not recommended to be modeled using this empirical approach